The value of stable isotope applications to identify the origin and fate of NO_3^- in small catchments

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Summary

In the last decades we have witnessed an increase in the nitrogen pollution of water resources worldwide. High nitrate accumulation in drinking water resources can be potentially dangerous to human health, but more specifically, it can reduce the environmental quality of terrestrial/aquatic ecosystems and increase the water management costs. Furthermore, nitrate accumulated in waterlogged soils stimulates microbial denitrification and thus, contributes to emissions of the greenhouse gas N_2O.

Since complex mountainous terrains represent about 20% of the world and provide fresh water to half of the humanity (Liniger et al., 1998), it is essential to study nitrate-N dynamics in terrestrial ecosystems, identifying non-point nitrate pollution sources in water and understand the fate/transformations of nitrate into the environment in these complex mountainous terrains. This could give us a better view of the total global nitrate-N cycle in catchments under the influence of different land use types, like forests and agroecosystems and also explore nitrate/N_2O relationships during the final phase of the nitrogen cycle.

The main focus of this thesis is (1) to quantify the proportional contribution of different nitrate sources to the export of nitrate from the Haean agricultural and two forest sub-catchments within the Soyang lake watershed in the northern part of South Korea as influenced by the monsoon precipitation regime. (2) Identify the origin/fate of nitrate export in the Haean agricultural and the two forest sub-catchments using nitrate $\delta^{15}N$ and $\delta^{18}O$ isotope abundance. (3) Improve the methodology to assess and distinguish between N_2O production from NO_3^- and N_2O consumption via further denitrification to N_2.

Considering summer rainfall inputs from a monsoon season (2103) with precipitations above the eleven years average (Kim et al., 2007) and an almost failed monsoon season (2014) with rainfalls clearly below the average, we develop scenarios for nitrate exports from forest and agricultural catchments in East Asian summer monsoon climate regions under conditions as predicted by global climate change scenarios. We also address a quantitative assessment of the N_2O production/consumption in waterlogged soils at a mountainous peat bog in the Czech Republic.

Heavy monsoon events, as in 2013, were the most pronounced drivers of nitrate leaching being responsible for more than 80 % of the nitrate output in the river runoff in both agricultural and forest sub-catchments. On the other hand, an almost missing summer monsoon in 2014 drove the

nitrate runoff in a different manner, being responsible for less than 1% of the total nitrate nitrogen river discharge in the previous year in both land use types.

Results of nitrate nitrogen and oxygen isotope abundance analyses suggest soil microbial nitrification as the most important contributor to the nitrate in the river runoff in the Haean agricultural and the forest sub-catchments. In addition, nitrate from groundwater, specifically in the agricultural land, and partially affected by microbial denitrification, contributed to the nitrate in the river runoff due to river-aquifer exchange fluxes especially after onset of the monsoon season.

In addition to nitrate from soil microbial nitrification wet atmospheric nitrate deposition played an important role especially at the mixed forest site, where it became a considerable source for the nitrate runoff after onset of the monsoon season. The deciduous forest showed better nitrate assimilation and retention capacities than the mixed forest. Despite higher nitrate concentrations as observed for the soil along depth profiles in parallel with higher soil pH values at the deciduous forest site nitrate losses by discharge were consistently lower than at the mixed forest site. In this thesis we confirm under field conditions a conceptual model developed by Nadelhoffer and Fry (1994), in which they postulated that nitrate from microbial mineralization and nitrification follows in its isotopic composition the soil total nitrogen isotope gradient. In our final study related with N_2O production/consumption we found that this waterlogged soil site was a sink for N_2O rather than a source. The relation of NO_3^- and N_2O isotope composition was complex with a combination of various processes along a soil depth gradient.

Our investigation shows that in extremely different monsoon seasons, as in 2013 and 2014, the nitrate leaching in the Haean agricultural and forest catchments was influenced by different hydrological and biogeochemical processes leading to different nitrate export scenarios during summer monsoon seasons. The simultaneous analysis of nitrate nitrogen and oxygen isotope abundances turned out as an elegant tool to separate the majority of these complex processes.

Zusammenfassung

In den letzten Jahrzehnten haben wir weltweit einen Anstieg der Stickstoffbelastung der Wasserressourcen erlebt. Eine hohe Nitratakkumulation in den Trinkwasserressourcen kann für die menschliche Gesundheit potenziell gefährlich sein, insbesondere jedoch die Umweltqualität terrestrisch/aquatischer Ökosysteme verringern und die Wassermanagementkosten erhöhen. Weiterhin stimuliert Nitrate in feuchten Böden die mikrobielle Denitrifikation und trägt so zur erhöhten Emission des Treibhausgases N_2O bei.

Da komplexe Gebirgsregionen etwa 20% der Erdoberfläche ausmachen und die Hälfte der Menschheit mit Trinkwasser versorgen (Liniger et al. 1998), ist es wichtig, die Nitrat-N-Dynamik in terrestrischen Ökosystemen zu untersuchen, nicht-punktförmige Nitratquellen im Wasser zu identifizieren und das Schicksal sowie den Umsatz von Nitrat in den Ökosystemen dieses komplexen gebirgigen Terrains besser zu verstehen. Damit könnten wir einen besseren Überblick über den gesamten globalen Nitrat-N-Zyklus in Einzugsgebieten unter dem Einfluss verschiedener Landnutzungstypen, wie Wald- und Agrarökosystemen, gewinnen und auch die Nitrat/N_2O-Beziehungen in einer weit fortgeschrittenen Phase des Stickstoffzyklus besser verstehen.

Das Hauptaugenmerk dieser Arbeit ist (1) die Quantifizierung des proportionalen Beitrags verschiedener Nitratquellen zum Nitrataustrag aus dem landwirtschaftlich geprägten Haean-Einzugsgebiet und zweier Waldeinzugsgebiete in der Lake Soyang Region im nördlichen Teil von Südkorea. (2) Die Identifikation der Herkunft und des Schicksals von Nitrat im agrarisch geprägten Einzugsgebiet von Haean und den beiden Waldeinzugsgebieten unter Zuhilfenahme der Stickstoff- und Sauerstoffisotopenhäufigkeit von Nitrat. (3) Die Verbesserung der Methodik zur Bewertung und Unterscheidung der Prozesse bei der N_2O-Bildung aus NO_3^- und des N_2O-Verbrauchs bei der weiteren Denitrifikation zu N_2.Unter Berücksichtigung eines extrem hohen Niederschlags während des ostasiatischen Sommermonsuns 2013 mit Niederschlägen weit über dem elfjährigen Durchschnitt (Kim et al. 2007) und eines fast vollständig ausgefallenen Sommermonsuns 2014 mit deutlich unter dem Durchschnitt liegenden Regenfällen, entwickeln wir Szenarien für den Nitrataustrag aus Wald- und landwirtschaftlichen Einzugsgebieten unter Bedingungen, wie sie von globalen Klimawandelszenarien für Regionen mit Sommermonsun vorhergesagt werden. Darüberhinaus beschäftigen wir uns auch mit einer quantitativen Bewertung der N_2O-Produktion und des-Verbrauchs in wassergesättigten Böden in einem gebirgigen Torfmoor in der Tschechischen Republik.

Starker Monsunregen im Jahr 2013 warder Hauptgrund für einen hohen Nitrataustrag. Mehr als 80% des Nitrataustrags fanden sowohl im landwirtschaftlich geprägten als auch in den beiden Waldeinzugsgebieten mit dem Monsunregen statt. Ein fast fehlender Sommermonsun im Jahr 2014 führte hingegen zu einem erheblich verringeren Nitratabfluss, der für beide Landnutzungstypen weniger als 1% des gesamten Nitratstickstoffaustrags im Vorjahr ausmachte. Die Ergebnisse der Nitratstickstoff- und -sauerstoff-Isotopenhäufigkeitsanalysen weisen darauf hin, dass die mikrobielle Nitrifikation im Boden in allen untersuchten Einzugegebieten der wichtigste Faktor für den Nitrataustrag im Abfluss verantwortlich war. Darüber hinaus trug Nitrat aus dem Grundwasser, das teilweise durch mikrobielle Denitrifikation beeinflusst war, aufgrund von Austauschprozessen zwischen Fluss und Grundwasser insbesondere in den landwirtschaftlichen Flächen bei Beginn der Monsunzeit zum Nitrataustrag bei.

Zusätzlich zum Nitrat aus der mikrobiellen Nitrifikation im Boden spielte auch der Nitrateintrag aus der atmosphärischen Deposition insbesondere im Mischwaldeinzugegebiet eine wichtige Rolle. Dort wurde er nach Beginn der Monsunzeit zu einer beachtlichen Quelle für den Nitrataustrag. Insgesamt war im Laubwald die Nitratassimilations- und –retentionskapazität höher als im Mischwald. Trotz höherer Nitratkonzentrationen im Bodenprofil und eines höheren Boden-pH-Werts war der Nitrataustrag aus dem Laubwald durchgängig niedriger als aus dem Mischwald. In dieser Arbeit bestätigen wir auch unter Feldbedingungen ein von Nadelhoffer und Fry (1994) entwickeltes konzeptionelles Modell, in dem sie postulierten, dass Nitrat aus der mikrobiellen Mineralisierung und Nitrifikation in seiner Isotopenzusammensetzung dem Isotopengradienten im Gesamtstickstoff des Bodens folgt. In unserer abschließenden Studie, die sich der N_2O-Produktion aus Nitratund dem N_2O-Verbrauch widmete, zeigte sich, dass der hier untersuchte wassergesättigte Moorkörper eher eine Senke für N_2O als eine N_2O-Quelle war. Die Beziehung in der isotopischen Zusammensetzung von NO_3^- und N_2O erwies sich als komplex mit einer Kombination verschiedener Prozesse entlang des Bodentiefengradienten.

Unsere Untersuchung zeigt, dass der Nitrataustrag in den untersuchten Agrar- und Waldeinzugsgebieten in extrem unterschiedlichen Monsunperioden, wie in den Jahren 2013 und 2014, durch unterschiedliche hydrologische und biogeochemische Prozesse beeinflusst wurde, die zu unterschiedlichen Nitrataustragsszenarien während des Sommermonsuns führten. Die simultane Bestimmung der Stickstoff- und Sauerstoffisotopenhäufigkeit im Nitrat erwies sich als elegantes Mittel zur weitgehenden Trennung dieser komplexen Prozesse.

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List of abbreviations

BaI_2	Barium iodide
$Ba(NO_3)_2$	Barium nitrate
BR	Brumiste
C:N	carbon nitrogen ratio
CO	Carbon Monoxide
DFG	Deutsche Forschungsgemeinschaft
FAO	Food and Agriculture Organization of the United Nations
H_2O	Water
HPLC	High-performance liquid chromatography
IAEA	International Atomic Energy Agency
KNP	Potassium, Nitrogen and Phosphorous
MAFRA	Ministry of Agriculture, Food and Rural Affairs
N	Nitrogen
NaI	sodium iodide
N2	Atmopsheric nitrogen
N2O	Nitrous oxide
NH4+	Ammonium
NO	Nitric oxide
NOx	Nitrogen oxides
NO3-	Nitrate
NK	Nitrogen Potassium
pH	Hydrogen potential
SENESCYT	National Secretary for Higher Education Science and Technology
TERRECO	Complex TERRain and ECOlogical Heterogeneity

WAMIS	Water resources management information system
WHO	World Health Organization

Chapter 1

Extended Summary

1. General Introduction

Almost the entire country of South Korea is composed of a heterogeneous mountainous landscape with complex and irregular topography. Due to the fact that 70% of the landscape is mountainous terrain (Bashkin et al., 2002), the remaining non-mountainous landscape fractions are not sufficient for cities and agricultural land. Thus, large mountainous areas are also under extensive agricultural use. East Asian monsoon with extreme precipitation regimes in summer time adds as a second hazard to the mountainous topography and makes natural and agricultural complex terrain ecosystems in this part of the world rather fragile. High precipitation events (monsoon), steep slopes, different flow directions, high erosion rates, land use change, mountainous agriculture, high river discharge rates that carry large amounts of sediments and contaminates, as nitrate, imply a large hazard to water quality and other ecosystem services. Therefore, nitrate source identification is a priority for the decision makers in South Korea. Simultaneously, this part of the world is a perfect location to improve our understanding of nitrate-N dynamics in both forest and agroecosystems.

1.1 Nitrate-N inputs and generation in complex terrains under the influence of East Asian monsoon season

Nitrate input and generation in ecosystems mostly has different origins. In natural ecosystems, microbial mineralization and nitrification are responsible for the nitrate available in soils (Vitousek and Howarth, 1991). Nitrate from nitrification of organic N needs ammonium (NH_4^+) as source material. Ecosystems can have high nitrification rates with simultaneously low ammonium and nitrate concentrations in the soil. This can be explained by the fact that nitrate is highly mobile and is taken up by plants, leached from soils or even denitrified as fast as it has been produced (Chapin et al., 2002). This panorama changes when we observe ecosystems with high atmospheric nitrogen deposition, in which nitrification rates can increase by 25% (McNulty et al., 1990). Inputs of atmospheric nitrate-N to ecosystems free of anthropogenic pollution are considered as rather small (Hedin et al.,

1995).On the other hand, anthropogenic activities increase these inputs in a way that nitrate-N of atmospheric origin can become the major nitrogen source for lots of ecosystems on the globe. Especially the emission of nitric oxides through fossil fuel combustion in industrialized countries is counted as directly responsible for at least 80% of the NO_X emissions that enter as the follow-up product nitrate into the nitrogen cycle (Delmas et al., 1997; Galbally, 1985; Logan, 1983). Therefore, high atmospheric nitrate deposition is common in highly populated and industrialized countries, like South Korea.

High atmospheric nitrate-N deposition affects mostly natural pristine ecosystems. For example, in forested watersheds nitrate-N deposition can contribute to: (1) nitrogen saturation, (2) changes in microbial mineralization and its subsequent nitrification, as a secondary process that increases while nitrogen availability begins to saturate plant/tree demand (Aber et al., 1998; Gundersen et al., 1998) and (3) the subsequent increase in nitrate leaching from soils (Aber et al., 1998, 1989; Stoddard, 1994; Vitousek et al., 1997). Atmospheric nitrogen wet deposition in complex mountainous terrain is known to be higher and increases with the altitude on hills and mountains due to major precipitation events (Lovett and Kinsman 1990). Therefore, summer monsoon season, counted as responsible for more than the 70% of the total rainfall per year in South Korea (Arnhold et al., 2013), can be considered as a large atmospheric wet nitrate deposition source.

Another important global nitrate input comes from synthetic fertilizers. They are counted as the main nitrate source in agroecosystems. Nitrate amounts drained into streams under the influence of agriculture are considered as higher than nitrate losses from forest ecosystems and urban areas (Fig. 1) (Sub-Global Assessments Working Group 2005). In South Korea fertilizer application is considered as the most important nitrate source affecting aquatic systems. Within the East Asian region South Korea is one of the heaviest mineral fertilizer users with 293 kg ha^{-1} yr^{-1}. The total mineral fertilizer amounts applied in the East Asian region is 445 kg ha^{-1} yr^{-1}, three times more than in South and Southwest Asia (Food and Agriculture Organization of the United Nations (FAO), 2014). The two most frequent forms of mineral fertilizers used in South Korea are ammonium and nitrate. Ammonium can be retained in the soil for longer time than nitrate, because it adsorbs to clay particles. However, under aerobic conditions ammonium is easily nitrified. Therefore, important nitrification

rates can occur in nitrogen rich agricultural soils (Chapin et al., 2002) followed by nitrate leaching into surface and groundwater (Mayer et al., 2001). Contrary, the direct use of nitrate as fertilizer makes it immediately susceptible to leaching due to its high solubility in water.

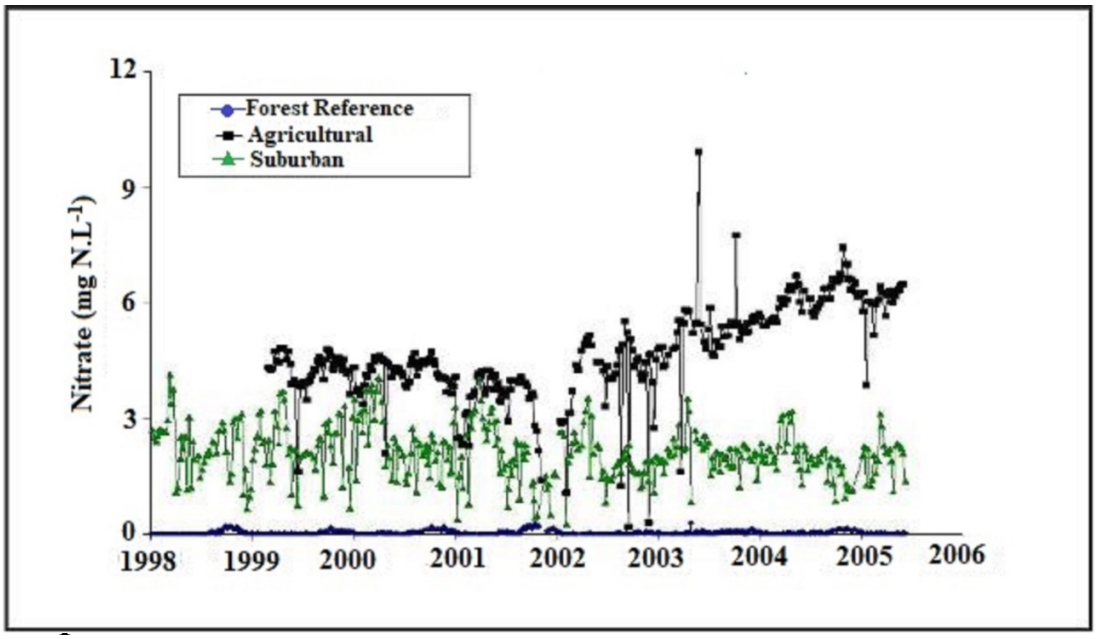

Fig. 1 Nitrate concentrations in streams draining from forested, suburban and agricultural watersheds in a long term (8 years) research monitoring (Groffman et al., 2004).

1.2 Nitrate-N losses from forests and agroecosystems in complex terrain under East Asian monsoon season

The initial indicators of N enrichment in forest watersheds and agroecosystems are: (1) the leaching of nitrate from soil into river and groundwater (Driscoll et al., 2003; Stoddard, 1994) and (2) the transformation and transfer of nitrate-N into the atmosphere as NO, N_2O or N_2 by microbial denitrification once nitrogen additions exceed biotic requirements (Galloway et al. 2003):

1. Large amounts of nitrate from synthetic fertilizers in agroecosystems, or atmospheric nitrogen deposition in forested watersheds transported into groundwater, streams and lakes can cause severe problems, as eutrophication, biodiversity loss (Smil, 1999) and human health risks (methaemoglobinaemia, cancer). Nitrate leaching depends directly on the

amount and sources of nitrogen inputs, precipitation, type of soil and land use (Boumans et al., 2008, 2005; Di and Cameron, 2002). In forest ecosystems nitrate leaching is considered as a direct response to chronic atmospheric nitrogen deposition (Aber et al., 1989; Aber and Magill, 2004; Adams et al., 2004; Creed and Band, 1998; Driscoll et al., 2003; Magill et al., 1997; Stoddard, 1994; Vitousek et al., 1979; Vitousek and Reiners, 1975) and is influenced by a variety of other factors, as vegetation type, retention capacities and flow paths (Lovett et al., 2002, 2000; Vitousek and Reiners, 1975; Williard et al., 1997). Also monsoon precipitation is one of the driving factors for excessive nitrate losses, especially in agricultural areas, which were found to be major contributors to nitrate losses at catchment scale (Kettering et al., 2012). Monsoon is also responsible for the well-studied hydrological flushing effect (Burns, 2005; Creed et al., 1996; Creed and Band, 1998) in forest ecosystems, where nitrate leaches from surface layers by a rising water table. In any case, nitrate losses are strongly depending on wetness conditions, storm events driven by monsoonal weather and hillslope elevation. About 60% of the N applied to agricultural sandy soils are considered to be lost to aquatic systems (Hansen and Djurhuus, 1996). In mountainous agricultural areas in South Korea, farmers add every year sandy soil on top of their fields to compensate for high erosion during the monsoon season.

2. The greenhouse gas N_2O is of special concern, because of its high global warming potential. Its emission due to microbial denitrification in natural ecosystems (60%) and ecosystems with influence of anthropogenic activities (mainly agroecosystems 40%) represent 121% since pre-industrial times (World Meteorological Organization, 2016). N_2O emissions from forest soils are influenced by soil moisture, temperature, soil type, tree species composition and atmospheric nitrogen deposition (Kesik et al., 2006; Menyailo and Huwe, 1999; Pilegaard et al., 2006; Skiba et al., 2009, 1998). In agroecosystems factors like amount of nitrogen fertilizer, type of crops and soils add to the factors mentioned above (Cole et al., 1997; Van Groenigen et al., 2010). On a global scale about 12% of the total nitrogen added is denitrified (Smil, 1999). In general terms all the nitrogen added to most agroecosystems is lost already within a year (Galloway et al., 2003). Therefore, Korean complex mountainous terrain together with the increase of soil temperature and the summer monsoon regime affect N_2O fluxes especially from agricultural soils (Berger et al., 2013b) and from groundwater where nitrate (mostly originating from fertilizers) is denitrified. All

the studied variables related with N_2O emissions from soils suggest in the first instance that South Korea would have conditions for high N_2O emission. Despite of the extreme moisture generated in the monsoon season and the amount of fertilizer or atmospheric deposition added to the soil, recent investigations, however, indicate that forests in the northern part of the country can act more as a sink of N_2O instead of a source, due to prolonged drought periods before monsoon season (Berger et al., 2013a, 2013b).

Although the main nitrogen input and turnover pathways in this complex mosaic of forest and agricultural ecosystems are identified, all the factors described above make the nitrate origin identification for water systems in South Korea rather complicated due to great variability in velocity and parallel occurrence of different biogeochemical processes. Identifying sources and biogeochemical processes behind the nitrate contamination in waters remains a conceptual and methodological challenge.

1.3 Stable Isotope approaches to identify nitrate sources and biogeochemical processes

The nitrate ion is composed of atoms belonging to two elements, nitrogen and oxygen. Each of these elements has a light and frequent isotope, ^{14}N and ^{16}O, and one or two heavier and rare isotopes, ^{15}N, ^{17}O and ^{18}O. Thus, nitrate isotope abundance analysis can either focus on nitrogen or oxygen isotope abundance or simultaneously on the isotope abundance of both elements.

Stable isotope abundance of nitrate has already frequently been used to identify nitrate sources in terrestrial and aquatic ecosystems. All these approaches make use of isotopic fractionations from sources to products that happen in chemical transformations during biogeochemical processes. Unfortunately natural nitrogen isotope abundance frequently has overlapping $\delta^{15}N$ ranges in different sources e.g. processes like atmospheric nitrate deposition and soil microbial nitrification cannot be separated free of doubt between each other and among other sources based on nitrogen isotope abundances alone (Kendall and McDonnell, 1998). These two biogeochemical processes also overlap the $\delta^{15}N$ composition of fertilizers and animal waste. However, natural $\delta^{15}N$ of nitrate resulting from animal waste is far more enriched than nitrate from soils without any fertilizer applications (Kreitler and Jones, 1975). Therefore, between fertilizer and animal waste we can find generally

distinctive $\delta^{15}N$ values. Microbial denitrification can also be identified by use of $\delta^{15}N$ natural isotope abundance and simultaneous nitrate concentration analysis. Decreases in nitrate concentration in aquifers alone can either be due to nitrate consumption during denitrification or dilution with low nitrate content waters. While dilution does not affect the nitrogen isotope composition, isotope discrimination in incomplete denitrification causes a characteristic ^{15}N enrichment in the remaining nitrate (Gormly and Spalding 1979; Mariotti et al. 1988; Böttcher et al. 1990).

The $\delta^{15}N$ values of nitrate from atmospheric deposition are usually in the range of −15‰ to +7‰ (Garten, 1996, 1992; Heaton et al., 1997; Hoering, 1957), and mineral fertilizers, main source in agroecosystems, have low $\delta^{15}N$ values due to their synthesis from atmospheric N_2 with a $\delta^{15}N$ value of 0% by definition (Kendall and McDonnell, 1998). Specifically nitrate fertilizers have mean $\delta^{15}N$ values between +2.75‰ and 0.76‰ (Hübner, 1986). Organic fertilizers, including animal waste, have a much wider range of $\delta^{15}N$ values (+2‰ to +30‰) (Kendall and McDonnell, 1998).

In the majority of soils ^{15}N isotope abundance ranges between -6‰ and +9‰ (Gebauer et al., 1994; Gebauer and Schulze, 1991). These values are affected by soil depth, vegetation, climate and land use history. Isotope abundance from agricultural soils that have been treated with mineral and organic fertilizers are specifically enriched in ^{15}N although both sources overlap $\delta^{15}N$ values of nitrate from precipitation and natural soils (Kendall and McDonnell, 1998). In depth gradients of undisturbed soils, $\delta^{15}N$ of total soil nitrogen tends to increase while simultaneously nitrogen concentrations decrease (Durka et al., 1994; Gebauer and Schulze, 1991; Nadelhoffer and Fry, 1994, 1988; Shearer et al., 1978).

Identification of nitrate sources is considered a real challenge when only $\delta^{15}N$ is used. Therefore, a dual stable isotope approach using simultaneously $\delta^{15}N$ and $\delta^{18}O$ of nitrate turned out as much more promising to separate atmospheric, terrestrial (Amberger and Schmidt, 1987; Durka et al., 1994; Kendall et al., 1996, 1995) and nitrogen fertilizer sources (Aravena et al., 1993; Aravena and Robertson, 1998; Wassenaar, 1995). In addition, this approach can also differentiate N_2O produced from microbial nitrification and denitrification (Wahlen and Yoshinari, 1985).

What makes the simultaneous analysis of nitrate $\delta^{15}N$ and $\delta^{18}O$ values more promising to distinguish the origin and fate of nitrate is the greater range in $\delta^{18}O$ values found in nitrate of different origins (80‰) corresponding to a smaller range in $\delta^{15}N$ values (30‰). The most positive $\delta^{18}O$ values occur in nitrate from atmospheric deposition ($\delta^{18}O$‰ = +25‰ to +76‰; Durka et al. 1994; Kendall 1998), because ^{18}O-enriched ozone is involved in the formation of atmospheric nitrate (Hastings et al., 2003; Johnston and Thiemens, 1997). The oxygen of nitrate in mineral fertilizers originates from atmospheric O_2 and thus, has $\delta^{18}O$ values close to +23.5‰ (Amberger and Schmidt, 1987). Due to their characteristic ^{18}O-enrichments nitrate from atmospheric deposition and nitrate in mineral fertilizers are clearly separated from nitrate originating from microbial nitrification. In microbial nitrification (conversion of NH_4^+ into NO_3^-) in soils two oxygen atoms originate from soil water and one from atmospheric O_2 with a constant $\delta^{18}O$ value of +23.5‰ (Andersson and Hooper, 1983; Hollocher, 1984; Kumar et al., 1983). The $\delta^{18}O$ value in soil water is driven by the $\delta^{18}O$ value of precipitation, which depends on the location and season of the rainfall. The $\delta^{18}O$ values in precipitation can be modelled for any location on earth by the Online Isotopes in Precipitation Calculator (Bowen, 2008). Therefore, the $\delta^{18}O$ value of nitrate from soil microbial nitrification can be calculated based on Eq. 1 (Amberger and Schmidt, 1987). Isotopic $\delta^{18}O$ values from microbial nitrification should be in the range of -2‰ and +6‰ (Kendall and McDonnell, 1998), although they can vary depending on the studied site (Amberger and Schmidt, 1987; Campbell et al., 2002; Durka et al., 1994; Mayer et al., 2001; Spoelstra et al., 2001). This theoretical approach of $\delta^{18}O$ calculation for nitrate from soil nitrification is based on the following assumptions: (1) the proportion of oxygen from water and atmosphere are the same in field samples as in laboratories, (2) no fractionation occurs during the incorporation of oxygen in the process and (3) the $\delta^{18}O$ values used by the microbes are identical to the bulk water from soil and the O_2 from atmosphere (Campbell et al., 2002). From here onwards any microbial process that uses nitrate is expected to fractionate both, oxygen and nitrogen atoms.

Eq. 1 $$\delta^{18}O(NO_3^-) = 2/3\ \delta^{18}O(H_2O) + 1/3\ \delta^{18}O(O_2)$$

Denitrification changes the isotopic composition of nitrate in a distinctive manner and enriches nitrogen and oxygen in a ratio of 2:1 (Amberger and Schmidt, 1987; Böttcher et al.,

1990). At the same time N_2O emitted from soils as product of microbial denitrification becomes depleted in ^{15}N when compared to the remaining nitrate. Thus, a negative correlation between the isotopic composition of nitrate and N_2O during ongoing denitrification should be expected. However, things may become also more complicated when considering that N_2O can be also further reduced to N_2 in denitrification or when soils switch from N_2O sources to N_2O sinks (Goldberg and Gebauer 2009a, b; Berger et al. 2013a). N_2O production, consumption or biological cycling in soils is controlled by the availability of nitrate as substrate and by diffusion conditions. It is currently debated to what extent scavenging of air-borne N_2O by soil microorganisms generates a major flux on an annual basis, but this research avenue can clearly contribute to clarifying the current imbalance in global N_2O budgets (Billings, 2008). The nearly 30% discrepancy between the known global N_2O sources and sinks could be partly explained by an underestimation of N_2O sinks in terrestrial ecosystems (Limpens et al., 2006). Natural $\delta^{15}N$ isotope abundance has been used to distinguish the production and consumption relationship of N_2O along soil profiles in different ecosystems (Novák et al., 2003, 1999). However, none of these studies simultaneously analyzed N isotope composition of co-existing NO_3^- and N_2O in the soil. Yet, complementary data from such an isotope analysis could help to distinguish between N_2O production from nitrate by denitrification, N_2O consumption by reduction to N_2, and scavenging of atmospheric N_2O by soil microorganisms along concentration gradients.

The powerful use of stable isotopes lies in their capacity of source and process identification: (1) organic vs. mineral fertilizers, (2) microbial denitrification vs. nitrification and (3) microbial nitrification vs. atmospheric nitrate deposition. Furthermore, stable isotopes are suited to identify the fate of nitrate in (1) surface waters vs. groundwater and (2) to separate N_2O production by denitrification in soils vs. consumption of N_2O either originating from denitrification or from the atmosphere.

2. Objectives

This study was carried out within the International Research and Training Group (DFG-IRTG) TERRECO (Complex TERRain and ECOlogical Heterogeneity). The group was composed of scientists with high level of expertise and great diversity of backgrounds as hydrologists, soil scientists, biologists and social-economists. The main objective of the

project was to provide science-based concepts that help local decision makers to develop plans for land management in mountain regions that lead to a sustainable water yield and improved ecosystem service quality. The specific objectives for this thesis are:

- Quantifying the proportional contributions of an agricultural and two forest sub-catchments to the nitrate export as influenced by different monsoonal precipitation regimes (Chapters 2 and 3).

- Identifying the biogeochemical and hydrological processes together with the origin and fate of nitrate export in the Haean agricultural sub-catchment using a nitrate dual isotope abundance approach in stream water and groundwater samples (Chapter 2).

- Comparing the fate of atmospheric nitrate deposition in a broadleaf and a conifer-dominated mixed forest catchment as influenced by monsoonal precipitation using a dual isotope approach (Chapter 3).

- Elucidating the isotope composition and concentration of nitrate along depth profiles of undisturbed forest soils and underlying biogeochemical processes (Chapter 3).

- Investigating relationships between isotope abundances of nitrate and N_2O along depth profiles of a peat bog and underlying biogeochemical processes (Chapter 4).

3. Hypotheses

1. Nitrate export from the agricultural catchment is much higher than nitrate export from the forest catchments.

2. Nitrate export from the agricultural and the forest catchments increases with increasing monsoonal precipitation intensities.

3. Fertilizers applied to the soils at the agricultural catchment, during growing season and before monsoon rainfalls, are being transported directly into the water systems due to a "Flushing effect" driven by the intense precipitation regime.

4. Microbial nitrification and denitrification are biogeochemical processes that are contributing as sources to the nitrate discharge, but in a lower rate than fertilizers in the agricultural basin, although they may play a major role at the forest sites.

5. Atmospheric nitrate deposition plays no major role as a direct source in the discharge runoff from the agricultural catchment, because the fertilizer application rates exceed the potential atmospheric nitrate contribution.

6. Atmospheric nitrate deposition plays a much greater role in the discharge runoff from the forested sites than from the agricultural catchment.

7. The mixed forest catchment is more vulnerable for nitrate loss by discharge runoff than the broadleaf forest catchment, due to a lower nitrate assimilation capacity of conifers.

8. In undisturbed soils nitrate isotope abundances and concentrations along depth profiles are positively correlated with total nitrogen isotope abundances and concentrations.

9. Nitrate and N_2O nitrogen isotope abundances in pore-water along depth profiles are negatively correlated.

4. General materials and methods

4.1 Sampling site 1 (Chapter 2 and 3)

The study was conducted in the northeastern part of South Korea within the Soyang lake watershed located in the Gangwon-do province, which is the largest water reservoir in the country (Kim et al., 2000), and it is the main source of drinking water for the 20 million metropolis Seoul (Fig. 2). The total area of the watershed is 2.675 km^2. Soyang lake watershed is dominated by

forested mountainous land (over 85%). Agricultural land has decreased due to urbanization within the watershed, while the highland agricultural area has increased. Despite the relatively small area compared to forested land, the agricultural area (mainly highland farming area) is considered as the most important nitrate contributor to the Soyang lake. The mean annual air temperature in this area is 10.5°C with minimum monthly temperature of -10°C in January and maximum monthly temperature of 27°C in August (1999 - 2013). Annual average precipitation is 1300 mm and between 50 – 60 % of the annual rainfall happens during the summer monsoon period (July – Sep) (WAMIS, 2014).

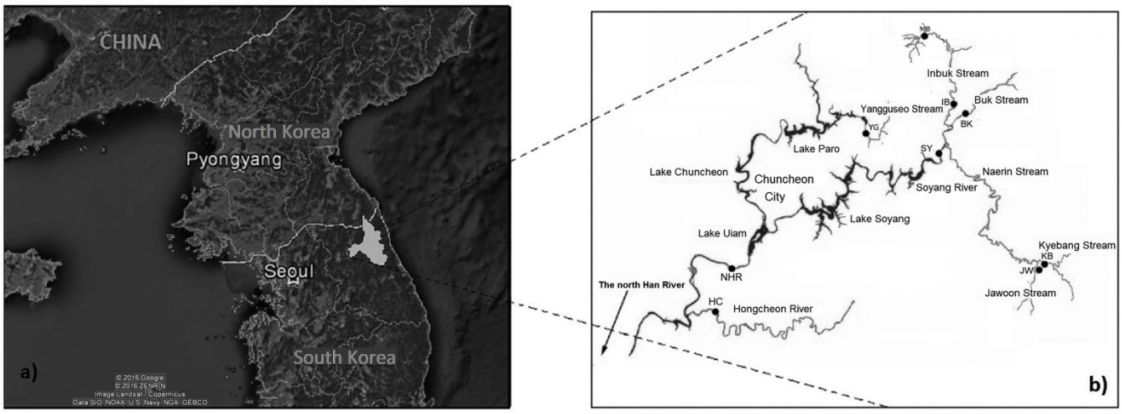

Fig. 2 Soyang lake watershed (b) located in the northeastern part of South Korea (a)

The first and in most detail studied sub-catchment within Soyang lake watershed was Haean-myun located in Yanggu–County (128° 5' to 128° 11' E, 38° 13' to 38° 20' N) (Fig. 3b). The punchbowl shaped basin has a total area of 64 km^2. It is the major farming territory of the entire watershed (Park et al., 2010) with about 30% area under agricultural land use (22% dry land fields and 8% rice paddies). 58% of the area are forested mountains and 12% are residential and semi-natural areas including grassland, field margins, riparian areas, channels, and farm roads (Arnhold et al., 2013). For our research, a river area within the sub-catchment was chosen as the most representative in terms of land use and water flow (Fig. 3c). The main dry land crops cultivated in the Haean catchment were in the years of the investigation primarily cabbage, potato, radish and soybean (7.8 %), orchards and ginseng (8.3%), and maize, pepper, rye, and sunflowers (4.1 % of the total catchment included as other dryland crop) (Maharjan, 2015).

Forest sub-catchments were chosen as complementary research sites. One of these forest sub-catchments is a pure deciduous forest within the Haean agricultural basin (Lat. 38.251532, N 128.11991 Long. W, 586- 1005 m asl) (Fig. 3d). The sub-catchment is dominated by tree species as *Juglans mandshurica, Acer pictum, Quercus dentata, Quercus mongolica,* and *Fraxinus rhynchophylla*. The entire deciduous sub-catchment area is 39.78 ha. The third studied sub-catchment is a mixed (coniferous/deciduous) forest located in Seohwa outside of the Haean agricultural basin (Fig. 3e), 6 km distance from the pure deciduous site (Lat.38.206828 N, Long. 128.185719 W, 368-682 m asl). The total area of the mixed sub-catchment is 15.6 ha with 6.1 ha of coniferous forest (39%) and 9.5 ha of deciduous forest (61 %). The mixed forest sub-catchment is dominated by coniferous trees including *Larix kaempferi* and *Pinus densiflora*, in the lower part of the basin. The upper part of the mixed sub-catchment is dominated by deciduous trees, including *Juglans mandshurica, Acer pictum, Quercus dentata, Tilia amurensis* and *Ulmus davidiana*.

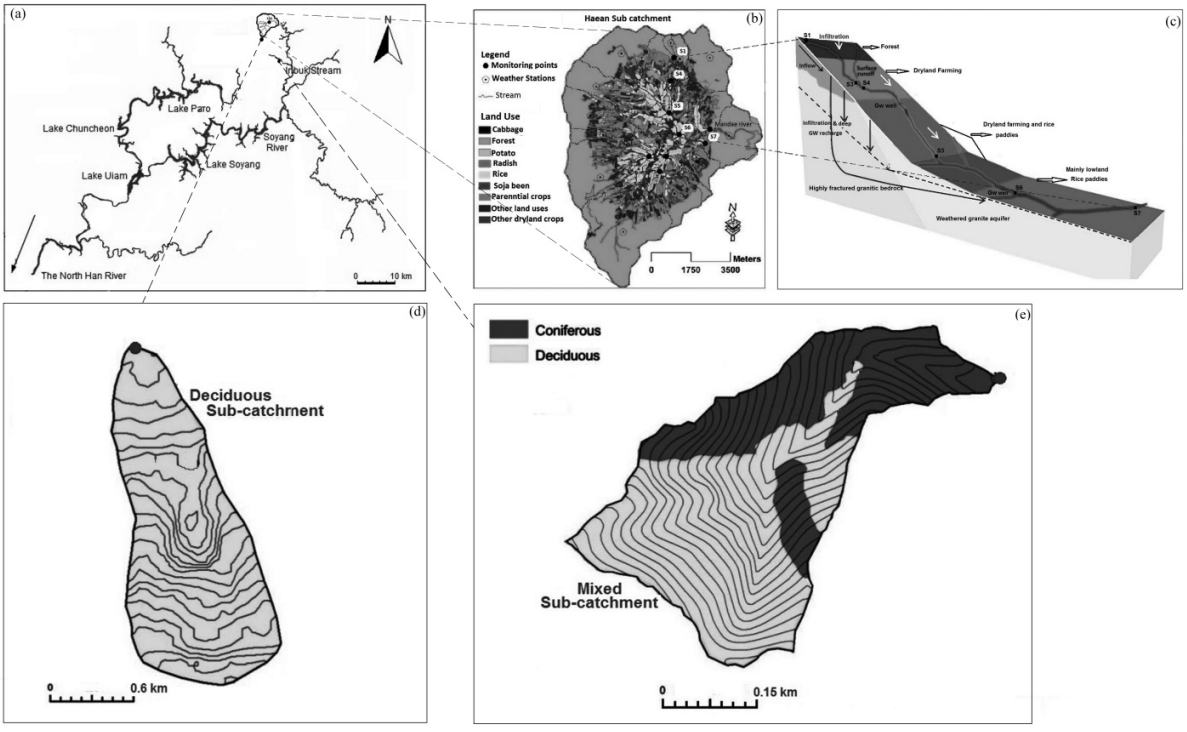

Fig. 3 Investigated sub-catchments within the Soyang lake watershed (a). A river area (c) within the agricultural Haean sub-catchment located in the northern part of the watershed (b) was chosen as the most representative in terms of land use and water flow. Complementary research was

conducted in a pure deciduous forest (d) located within the Haean sub-catchment and a mixed forest (coniferous-deciduous) located 6 km from Haean agricultural sub-catchment (e)

4.1.1 Field instrumentation, sample and data collection

The sampling design was made to determinate the influence of the precipitation regime and land use on the sources and total nitrate discharge from each sub-catchment. All the samples were collected every second day or after every rain event in the dry pre-monsoon season. During heavy monsoon season samples were collected after rain events up to every six hours in precipitation events that lasted at least 12 hours. Discharge was measured with V-notch weirs located in the outflow of each sub-catchment (Fig 4). In the agricultural sub-catchment additional measurements were taken with an electromagnetic device using the velocity-area method. Weather data and precipitation was measured with automatic weather stations and rain collectors located in each sub-catchment (Fig. 5).

Fig. 4 Weirs located in the investigated Haean agricultural sub-catchment (a and c) and the mixed (b) and deciduous (d) forest sub-catchments

In the Haean agricultural sub-catchment groundwater wells were installed perpendicular to the stream at different elevation zones of the altitudinal transect (Fig. 6) for groundwater sampling. In the forest sub-catchments extra instrumentation was installed: Autosamplers for automatic stream water sampling at the outflow of each forest. Throughfall collectors for rain water sampling. Cero tension plates (0-20 cm) and suction ceramic cups (30-60 cm) for soil water sampling at different depths. All samples were collected for nitrate concentration and stable isotope abundance analysis (Fig. 7).

Fig. 5 Weather stations (a) and rainfall collectors (b) recorded precipitation data and rain samples in the investigated agricultural Haean and forest sub-catchments.

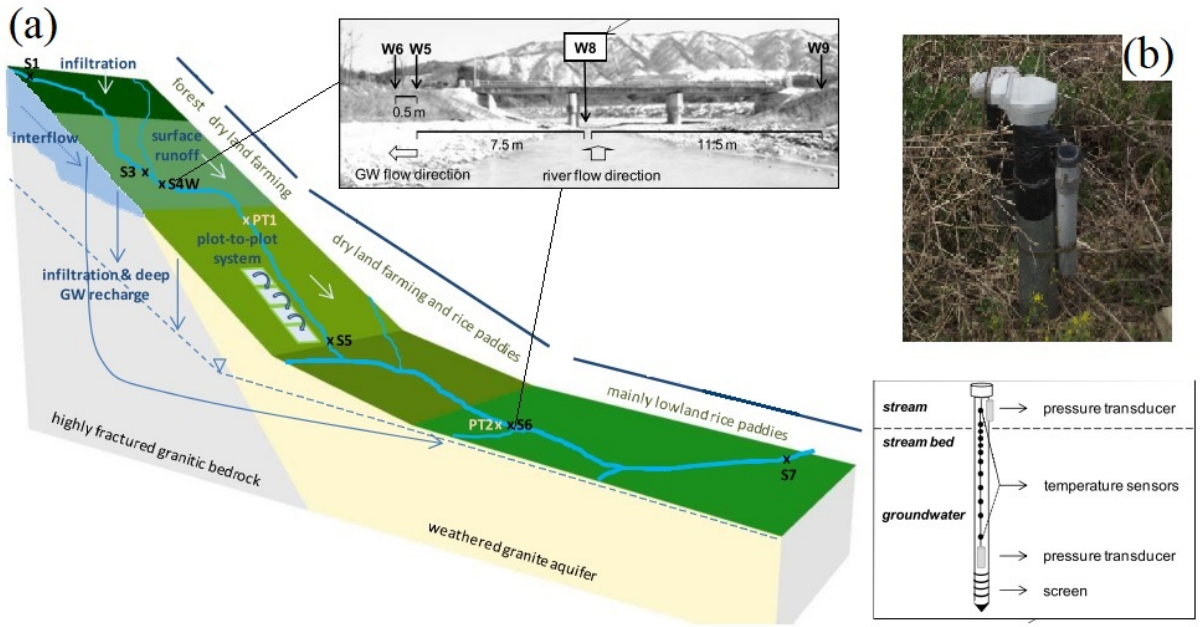

Fig. 6 Groundwater wells (b) installed at two sampling points in a different altitudinal gradient and under distinct land uses (a).

4.1.2 Laboratory analyses

Nitrate concentration

Rain, throughfall, stream water, groundwater and soil water samples were analyzed for nitrate concentrations using an anion exchange high performance liquid chromatograph (HPLC) and subsequent UV detection (HPLC LC4000 Jasco Europe S.r.l., Cremella, Italy). For further details of this method see Gebauer et al. (1984).

Sample preparation and isotope abundance analysis

Nitrate extraction from each water sample as described by Huber et al. (2011) was required before their subsequent isotope abundance analysis. Nitrate isolation consisted in the precipitation of $Ba(NO_3)_2$. A solution of NaI + acetone + hexane was added to each sample to separate insoluble compounds. After separation we added BaI_2 to the samples to the final precipitation of $Ba(NO_3)_2$. We dried aliquots of each sample into tin (for N isotope abundance analysis) or silver capsules (for O isotope abundance analysis) (Fig. 8).

Fig. 7 Equal equipment was installed in the forest sub-catchments. Throughfall collectors for rain samples (c). Cero tension plates (b) and suction ceramic cups (a) for soil water samples.

Relative nitrogen isotope abundances of the nitrate samples ($\delta^{15}N_{NO3-}$) were measured with an elemental analyzer (Carlo Erba 1108, Milano, Italy) coupled to an isotope ratio mass spectrometer (delta S, Finnigan MAT, Bremen, Germany). Nitrogen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard acetanilide with known nitrogen content of 10.36% (Gebauer and Schulze, 1991). Relative oxygen isotope abundances of the nitrate samples ($\delta^{18}O_{NO3-}$) were measured by thermal conversion through a pyrolysis system (HTO, HEKAtech, Wegberg, Germany) coupled to an isotope ratio mass spectrometer (delta V advantage, Thermo Fisher Scientific, Bremen, Germany) as described by Gebauer et al. (2016). Oxygen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard benzoic acid with known oxygen content of 26.20%.

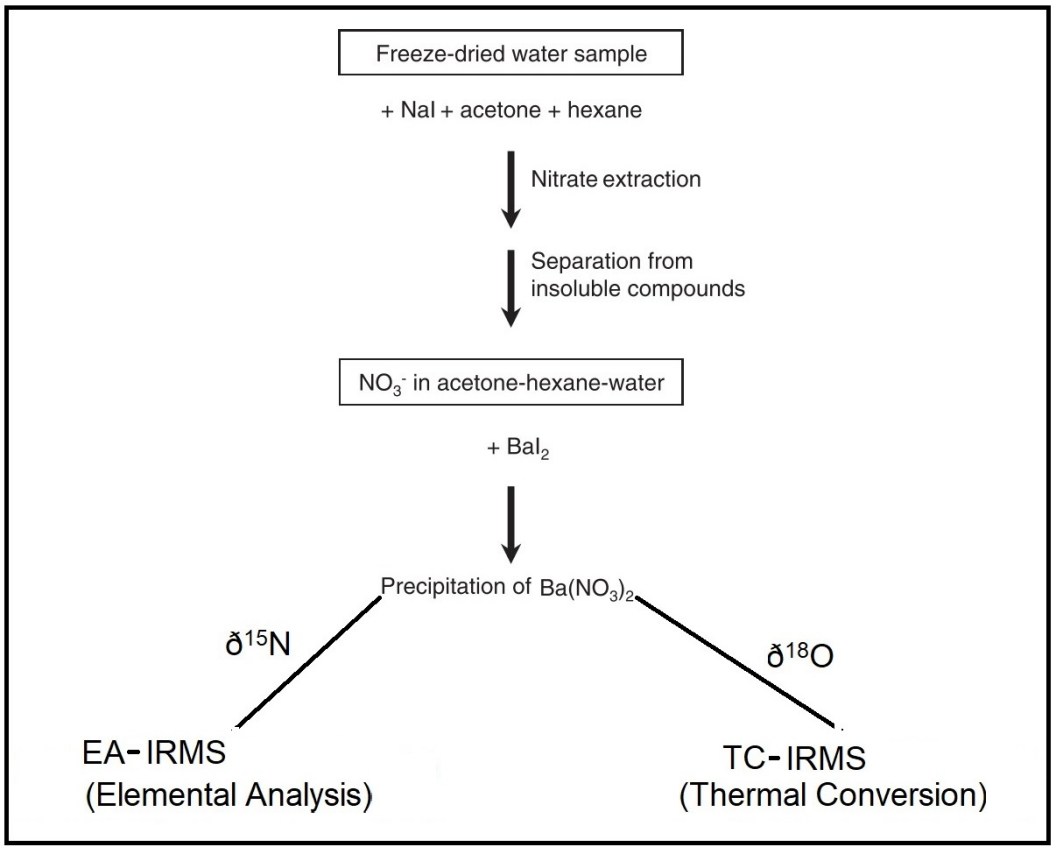

Fig. 8 Scheme of the nitrate isolation procedure

Nitrate fluxes and isotope calculations

Nitrate flux calculations were carried out using the calculated N_{NO3}^- from nitrate concentrations multiplied by the total stream area discharge and rain input per day. We calculated fluxes in rain input using bulk precipitation and throughfall data, because during heavy monsoon rainfall no major differences in nitrate concentrations of rain between under and out-canopy could be registered.

Stable isotope abundance results from nitrate in stream and groundwater were plotted together with the natural abundance of the major nitrate sources that may influence aquifers (Kendall, 1998), like microbial nitrification, denitrification and atmospheric deposition. A theoretical microbial nitrification was calculated to compare this source with the stream water, groundwater and soil water nitrate isotope abundance data in the research area (Eq. 1).

4.2 Sampling site 2 (Chapter 4)

The study was conducted in an ombrotrophic peat bog located on a mountain plateau of the Ore Mts. (Erzgebirge, Krusne hory) in the northwestern Czech Republic, Central Europe (Fig. 9). The bog's elevation is 930 m, and long-term annual precipitation averages 1080 mm. The unforested southern part of the bog is nearly 100 % Sphagnum covered, separated by dense, 2.5-m high dwarf-pine dominated vegetation. The entire wetland is surrounded by mature stands of Norway spruce which were moderately affected by acid rain (ca. 1970-1995). The bog is located 30 km upwind from a cluster of 11 coal-burning power plants that were a major source of acidifying SO_2 and NO_x gases.

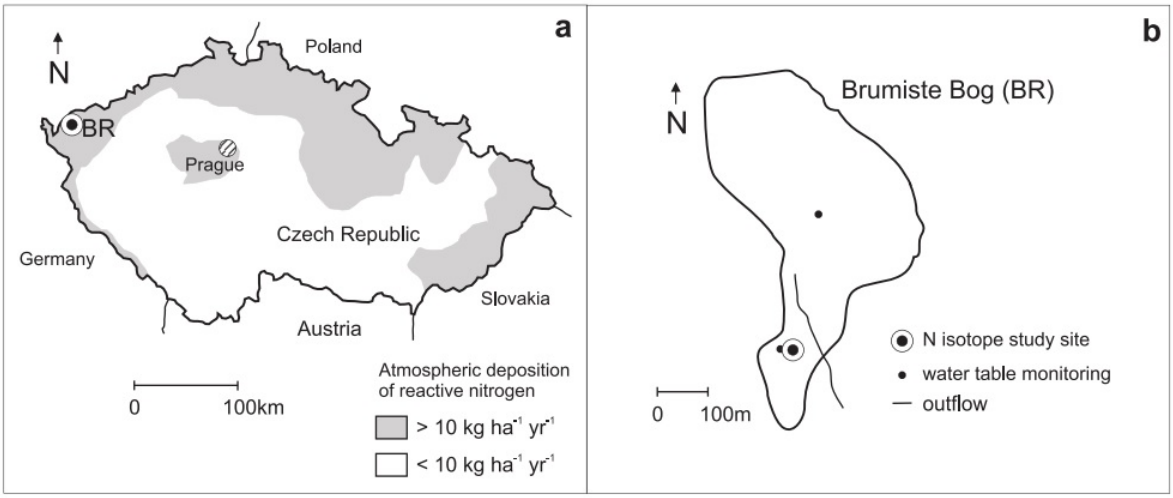

Fig. 9 Study site location. (a) The Brumiste Bog (BR) is situated 20 km west of the "Black Triangle" region near the state border between the Czech Republic, Poland and Germany. The N isotope study was conducted in a *Sphagnum* lawn (b) extending over the southern tip of BR.

4.2.1 Sampling

N_2O gas samplers

Six gas-sampler cylinders were installed in a circle at distances between 2.5 and 3 m to collect soil gas from the peat bog along a depth gradient (Fig. 11). Each sampler consisted of a 60 cm long PVC cylinder divided in six compartments, 10 cm in length. Each compartment was perforated by drill holes (diameter of 5 mm) in a 2.5.cm wide band in its center. For more details see Goldberg et al. (2008). Peat pore-water gas samples were taken through a tube connected on one end

to an evacuated 100 mL glass bottle and on the other end to an air bag filled with N_2 gas at ambient pressure. The gas sample volume extracted from the compartments at different depths was replaced by N_2 from the attached bag.

NO_3^- water samplers

Thirty six suction cups were installed to collect water samples from the peat bog at six different depths (10-60 cm). Six cups were located at 1 m distance from each gas sampler (Fig. 10). Each cup was made of ceramic material (porosity 48 vol. %, maximum) with a PVC tube long enough to reach the required peat depth. To collect samples, all suction cups were connected to a vacuum device, which allowed the solution from each cup to be transported by under-pressure to the bottles. The equipment was linked to a computer control system (Electronic Technical Center, University of Bayreuth), which kept a nearly constant under-pressure (HS260P-30 Black Swan, Hanover Solar GmbH, Germany). For more details see Göttlein et al. (1996), Göttlein and Matzner (1997). In all, 36 N_2O and 36 NO_3^- samples were collected from six replicates at six different depths.

4.2.2. Analysis

The pore-water gas samples from different peat depths were analyzed for N_2O concentration and N isotope abundance ratios. We used a gas chromatograph–isotope ratio mass spectrometer coupling with a pre-GC concentration device. As a laboratory standard, N_2O gas (99.997 %, Rießner, Lichtenfels, Germany) was used previously calibrated with N_2 and N_2O reference gas. N_2O concentrations were calculated from the volume of the gas samples and the peak area on m/z 44 using a calibration curve. For further details see Goldberg et al. (2008) and Berger et al. (2013).

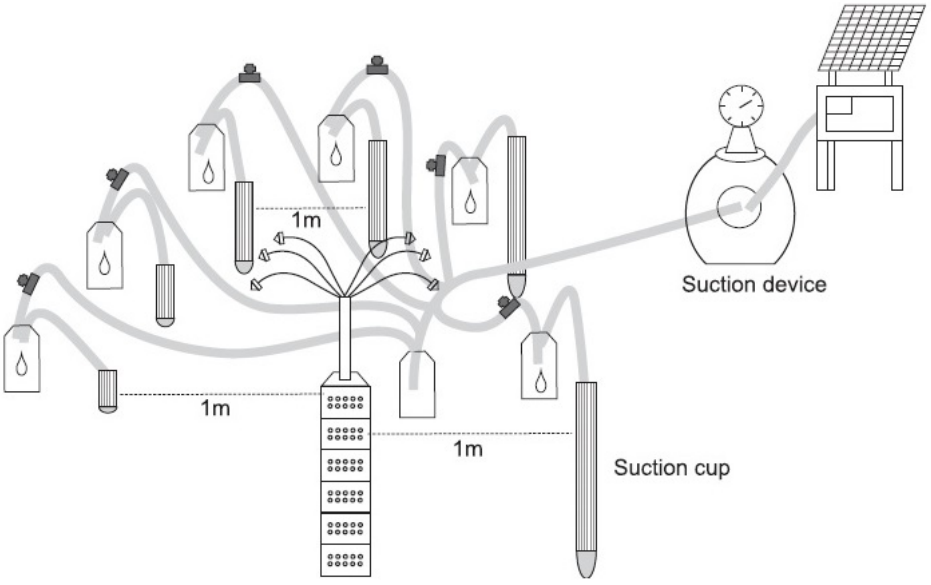

Fig. 10 Design and installation of equipment in the peat bog for collection of gas (gas cylinder located in the center of the installation) and water samples (six suction ceramic cups located around the gas sampler) connected to an automatic vacuum system.

Laser absorption spectroscopy was used for the determination of oxygen stable isotope ratios in peat pore water. The $^{18}O/^{16}O$ isotope ratios were expressed in the $\delta^{18}O$ notation as a relative ‰ deviation from an agreed-on standard (V-SMOW).

Samples of atmospheric deposition and runoff were analyzed for NH_4^+ concentrations by spectrophotometry (Perkin-Elmer 200 Hitachi, 2 SD of 4.4 %), and for NO_3^- concentrations by liquid chromatography (Knauer 1000, 2 SD of 3.8 %). For N isotope analysis, 500 mL of atmospheric deposition or peat porewater were concentrated on Dowex 50W and Dowex 1 x cation and anion exchange resins, and separated into NH_4^+ and NO_3^-. Solution aliquots were made alkaline with MgO and steam-distilled into a small excess of diluted H_2SO_4 (Bremner, 1965). Prior to distillation, Devardas alloy was added for NO_3^- analysis. The resulting ammonium sulfate was dried and analyzed for N isotope ratios. A Fisons 1108 elemental analyzer was connected to a Finnigan MAT 251 mass spectrometer (Bremen, Germany) to measure the N isotope composition. The $^{15}N/^{14}N$ isotope ratios are expressed in the $\delta^{15}N$ notation as a relative ‰ deviation from an agreed-on standard (atmospheric N_2). The 2 SD reproducibility for N isotopes in water was 0.2‰.

5. Thesis outline

In chapters 2 and 3 nitrate fluxes and sources were examined and identified in: 1) an agricultural sub-catchment and 2) in a deciduous and a mixed forest sub-catchment under the influence of two extremely different monsoon seasons. Nitrate inputs by atmospheric nitrate-N deposition were similar in all sub-catchments, but different between years 2013 and 2014. In the forest sub-catchments 90% of the nitrate-N rain input was during monsoon in the growing season 2013. In the following year (2014) the lack of monsoon affected nitrate-N deposited by rain, which represented only 40% of the year before (2013). The deciduous forest acted as a sink of nitrate-N, because total nitrate-N atmospheric deposition was 2.5 times higher than the N_{NO3}^- discharge. On the other hand, the mixed forest showed a lower retention capacity than the deciduous forest (confirming hypothesis 7). In the Haean agricultural sub-catchment atmospheric nitrate-N deposition represented only 5.2% in 2013 and 0.7% in 2014 in relation to the synthetic fertilizer applications in the area (313 kg N ha^{-1} y^{-1}) confirming hypothesis 5.

Nitrate-N exports were higher from the agricultural Haean sub-catchment than from the forest sites (confirming hypothesis 1). Monsoon was directly related with the nitrate export in all sub-catchments. Nitrate-N leaching from the Haean agricultural sub-catchment during the monsoon season 2013 represented 90% of the total nitrate discharge. In the mixed forest catchment nitrate leaching was affected by the monsoon precipitation, where 80% of the nitrate discharge was during this period. More stable nitrate export was observed in the deciduous forest where 50% of the nitrate-N discharge was during monsoon season. Thus, hypothesis 2 was partially confirmed. In the Haean agricultural sub-catchment nitrate concentrations in stream were (0.4 – 64.1 mg L^{-1}) higher than in the forest sites (6.5 – 26.7 mg L^{-1}). The highest values were recorded in groundwater under the influence of dry-land crops. The results of nitrate identification indicated that nitrate of microbial nitrification was the main nitrate source in stream water in all sub-catchments. In the Haean agricultural sub-catchment denitrification occurred in the groundwater, which contributed to the river discharge especially after onset of the monsoon season, due to aquifer connectivity. In the mixed sub-catchment direct contribution from atmospheric nitrate was observed during monsoon season, which lead us to partially accept hypothesis 6. In the deciduous forest microbial nitrification was the only nitrate source observed during the growing season. We rejected the hypotheses 3 and 4.

Nitrate concentrations collected along soil depth gradients (10-60 cm) in the forest soils, showed lower values in the mineral soil (50 and 60 cm) of the mixed and of the deciduous forest. The organic layer (0-20 cm) had higher nitrate concentrations in both forest sub-catchments, although in the deciduous forest we observed significantly higher nitrate concentrations than in the mixed forest. Negative and significant correlations between nitrate concentration and $\delta^{15}N_{NO3}^-$ with soil depth were found in both forests. Significate differences in $\delta^{15}N_{NO3}^-$ values were observed between organic and mineral layers in both studied sites. This finding indicates that nitrate collected in the various soil depths always originated from nitrification of organic matter in the respective soil depth and was always associated with the same isotope fractionation.

The $\delta^{15}N$ values of soil total nitrogen (literature data from the same forest sites) increased from the organic layer to the mineral soil of the deciduous and mixed forest. This increase in $\delta^{15}N$ of soil total nitrogen ran mostly in parallel with our depth gradient in $\delta^{15}N_{NO3}^-$ for both investigated forest sites. Soil nitrate from identical positions along the gradient was consistently more depleted in $\delta^{15}N$ than soil total nitrogen, confirming hypothesis 8.

Previous research in soils of the agricultural Haean sub-catchment observed low N_2O emissions, which had two possible explanations: 1) further denitrification of N_2O to N_2 or 2) large amounts of the highly mobile NO_3^- leached before denitrification (Berger, 2012). In this thesis we observed high amounts of nitrate-N in the river and groundwater, which may explain the low N_2O emissions from soil at the Haean sub-catchment. Still, additional investigation was needed in aim to understand in a mechanistic way, how N_2O emissions from soils occur during further denitrification into N_2, and if NO_3^- and N_2O are coupled through denitrification, or de-coupled as a result of microbial scavenging of atmospheric N_2O.

. In chapter 4 we assess N_2O production and consumption in a waterlogged soil. We used nitrogen stable isotopes of N_2O and NO_3^- in aim to distinguish between N_2O diffusion in pore water, N_2O production from NO_3^- *via* denitrification, and N_2O consumption *via* further reduction to N_2. Nitrous oxide concentrations in the atmosphere were nearly 20 % higher than in peat pore water gas, suggesting that the wetland served as a sink for air-borne N_2O, rather than a N_2O source. Following a soil depth gradient, nitrate-N between atmospheric input and runoff, indicated an export of secondary residual nitrate. At a depth of 10-20 cm, nitrate-N was isotopically identical to the atmosphere. At 60cm isotope values were identical to the runoff. N_2O concentrations were constant

through the profile with higher $\delta^{15}N$-N_2O values upcore and a strong negative correlation between $\delta^{15}N$ values of nitrate and nitrous oxide in the 60-30 cm interval, which could not be explained by a single denitrification step. We suggest that the relatively high $\delta^{15}N$ values of nitrate in the deepest peat layer reflected higher rates of NO_3^- reduction, compared to the 30 cm depth, and that the progressively heavier N_2O-N upcore corresponded to residual N_2O following partial reduction to N_2, along with an increasing proportion of atmospheric N_2O in the pore water. These results lead us to partially accept the hypothesis 9.

Further results of the three investigations are listed below within the synopsis of each chapter.

5.1 Nitrate runoff in the Haean agricultural sub-catchment: Comparison of two extremely different monsoon seasons (Chapter 2)

The monsoon season in South Korea has a great influence on the biogeochemical and hydrological processes in the entire country, but is specifically of concern in the Soyang lake watershed, the main drinking water reservoir for the 20 million metropolis Seoul. Consequently, control of water quality and especially nitrate concentrations in lake Soyang is of high public priority. The watershed has a complex terrain with different types of land uses, including intensive agricultural management. The Haean sub-catchment is the most prominent agriculture-dominated basin of the Soyang lake watershed. It is composed of a forested belt in the steep top slopes of the bowl-shaped basin, followed by a dry-land agriculture belt in the bottom-slope areas and rice paddies at the bottom of the basin.

In areas with only one recognizable nitrate source the calculation of total nitrate exports might be sufficient for an effective decision making. However, in areas with complex terrain, extreme weather events and non-point nitrate sources, like in the Haean basin, a simple nitrate export mass balance would not be sufficient to elucidate in a mechanistic manner the origin of nitrate exports. Additional information on biogeochemical key processes in the nitrogen cycle is required. Therefore, stable isotopes are a useful tool to quantify and determinate the origin of nitrate inputs into lake Soyang. The $\delta^{15}N$ values of nitrate from different sources often show overlapping ranges, but the additional measurement of the $\delta^{18}O$ values allows a more precise classification (Deutsch, 2006; Durka et al., 1994; Mayer et al., 2002). According with this principle the nitrate

derived from sewage or manure or fertilizes is isotopically distinct between each other and from the other sources and processes as microbial nitrification and denitrification.

With a sampling design made to determinate the influence of the precipitation regime and the land use in the nitrate discharge, river water samples, and rain samples were taken before and during the monsoon season to analyze the nitrate concentration, and $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ abundance in each phase of the nitrogen cycle. The sampling years 2013 and 2014 were particularly different among each other, especially in terms of intensity and frequency of rain events. Data from amount of rain and river discharge were taken to quantify the proportional contribution of nitrate from this sub-catchment during both growing seasons. This data base together with the climate information helped showing how the monsoon season behaves and how differences in the monsoon intensity can influence the isotope signatures in the Haean agricultural valley.

Heavy monsoon events, as in 2013, were the most pronounced drivers of nitrate leaching being responsible for more than 80 % of the nitrate output in the river runoff. On the other hand, an almost missing summer monsoon in 2014 drove the nitrate runoff in a different manner, being responsible for only 0.4% of the total nitrate nitrogen river discharge of the previous year. Results of nitrate nitrogen and oxygen isotope abundance analyses suggest soil microbial nitrification as the most important contributor to the nitrate in the river runoff. In addition, nitrate from denitrification in groundwater, specifically from the dry land areas, contributed to the nitrate in the river runoff due to river-aquifer exchange fluxes especially after onset of the monsoon season. Direct leaching of nitrate from mineral fertilizers applied in the area and atmospheric nitrate deposition were obviously only minor contributors to the nitrate in the river runoff. Our investigation shows that in extremely different monsoon seasons, as in 2013 and 2014, the nitrate leaching in the Haean agricultural catchment was influenced by different hydrological and biogeochemical processes leading to different nitrate export scenarios during summer monsoon.

5.2 The fate of monsoonal atmospheric nitrate deposition in two forest catchments: A mass balance and stable isotope approach (Chapter 3).

South Korea has about 70% mountainous area (MAFRA, 2013), and the total forest land use is about 64.1% (Korean Forest Service, 2013). Deciduous forest represents 27% of the total forest

land, while coniferous and mixed forests are 41% and 29%, respectively (Kim et al., 2017; Korean Forest Service, 2013). Great parts of the forested areas in this country are located in catchments surrounding highly populated cities, like the metropolis Seoul.

The main anthropogenic nitrate-N source for natural and semi natural forests is wet atmospheric deposition (Aber et al., 2003). The nitrogen additions in areas unaffected by industrial sources should be smaller than 2 kg N ha^{-1} yr^{-1} (Aber et al., 1989; Lovett et al., 1982). On the other hand nitrate deposition in forest areas influenced by anthropogenic activities in densely populated and industrialized regions can reach 40 kg N ha^{-1} yr^{-1}. Therefore, atmospheric nitrate deposition may play an important role in biogeochemical processes and nitrate discharge, especially in the Soyang lake watershed, located 140 km northeast from the 20 million metropolis Seoul (Arnhold et al., 2014; Berger et al., 2013b; Kettering et al., 2013).

A dual stable isotope approach, which uses $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ signatures, is a powerful tool to identify nitrate sources that can overlap when solely $\delta^{15}N_{NO3-}$ is used. The $\delta^{18}O_{NO3-}$ values are especially useful for differentiating between nitrate deposited from the atmosphere and nitrate formed by microbial nitrification. The formation of nitrate in the atmosphere involves exchange of oxygen atoms with ozone, which has a high $\delta^{18}O$ value (Curtis et al 2011). In contrast, nitrate formed by microbial nitrification derives two of its oxygen atoms from water, which has a low $\delta^{18}O$ value. (Curtis et al. 2011). In other words, microbial nitrification uses two oxygen atoms come from water and one from the atmosphere (Andersson and Hooper, 1983; Hollocher, 1984; Kumar et al., 1983). In this investigation we measured nitrate concentrations of stream water, rain and soil water and $\delta^{15}N$ and $\delta^{18}O$ isotope abundance of stream and soil water. For the first time, we confirm under field conditions the conceptual model developed by Nadelhoffer and Fry (1994), in which they postulated that nitrate from microbial mineralization and nitrification follows in its isotopic composition the soil total nitrogen isotope gradient.

Extremely different summer monsoon seasons drove the nitrate discharge from the deciduous and mixed (deciduous-coniferous) forest sub-catchments in the Soyang lake watershed. Total nitrate-N export was closely related with the rainfall events and intensity in both years. The nitrate-N discharge runoff at the deciduous forest was lower than the atmospheric nitrate-N deposition at this site, thus sink conditions characterized the deciduous forest during growing the seasons 2013 and 2014. Nitrate-N discharge runoff at the mixed forest was six times higher than the atmospheric

nitrate-N deposition in both years. Nitrate was the most important nitrogen ion in the discharge runoff over NH_4^+ (Lee et al., 2016) in both sites and years. Nitrate $\delta^{15}N$ and $\delta^{18}O$ isotopic composition of stream water from both forests revealed microbial nitrification as the main nitrate source in the discharge runoff during both summer monsoon seasons. Specifically in the mixed forest, atmospheric nitrate deposition contributed as an extra nitrate source for the discharge runoff at the onset of the monsoon season 2013. No direct response from atmospheric deposition in the stream runoff at the deciduous forest was found. Thus, this forest had probably better retention capacities then the mixed forest (Gebauer and Schulze 1997; Magill et al. 1997; Lovett et al. 2000). Despite higher nitrate concentrations as observed for the soil along depth profiles in parallel with higher soil pH values at the deciduous forest site due to most probably higher microbial mineralization and nitrification rates (Pardo et al. 2007) the nitrate retention capacities of the deciduous forest site were higher than at the mixed forest site. Nitrate $\delta^{15}N$ in soil solution followed the same depth gradient as $\delta^{15}N$ of soil total nitrogen. Furthermore, nitrate concentrations in the soil solution decreased with increasing depth indicating lower nitrification in the mineral soil than in the organic layer. This finding of characteristic nitrate isotope depth gradients could probably only be realized in a dry monsoon season as in 2014. Otherwise soil water movement due to frequent rainfall would have interfered with gradients built up by biogeochemical processes, like microbial nitrification.

5.3 Relationship between nitrogen isotope ratios of NO_3^- and N_2O in vertical pore-water profiles through a polluted rain-fed peat bog (Chapter 4)

Assessments of N_2O production and consumption in waterlogged soils are needed for the formulation of efficient mitigation strategies and assess the global N_2O budgets which currently have a 30% imbalance between the known global sources and sinks. It is on debate to what extent scavenging of air-borne N_2O by soil microorganisms generates a major flux on an annual basis. The balance between N_2O production, emission and biological cycling in the soil is controlled by the availability of the NO_3^- substrate and carbon skeletons as electron donors, enzymatic activity of the denitrifying community, and diffusion conditions (Berger et al., 2017; Hill et al., 2016; Morley and Baggs, 2010).

Sources and sinks of various species of reactive nitrogen in soils can be localized, and sometimes also quantified, by measurements of $^{15}N/^{14}N$ isotope ratios (Nadelhoffer and Fry, 1988). We report on measurements of a combination of $\delta^{15}N_{NO3-}$ and $\delta^{15}N_{N2O}$ values along vertical pore-water profiles in an ombrotrophic, high-elevation peat bog in the Czech Republic (Central Europe). Vertical peat profiles often exhibit a down-core shift to isotopically heavier N (i.e., to higher $\delta^{15}N$ values), resulting from preferential mineralization and export of the light isotope ^{14}N from deeper and older peat layers (see chapter 5.2, Kohzu et al., 2003; Novák et al., 1999). Production of N_2O by denitrification is characterized by a large N-isotope shift towards the isotopically lighter product (Goldberg et al., 2008). The residual NO_3^-N is considered to become progressively enriched in the heavier isotope ^{15}N (see chapter 5.1). Currently available methodologies do not permit direct measurements of the $\delta^{15}N$ signature of N_2O emitted from waterlogged and aerated/rewetted soils, because extremely long sampling times would be required. Instead, recent studies have provided insights into N_2O production/consumption by measuring $\delta^{15}N$ values of N_2O dissolved in peat bog pore-water along depth profiles (Goldberg et al., 2008; Novak et al., 2015). None of these studies, however, simultaneously analyzed N isotope composition of co-existing NO_3^- and N_2O in the pore-water. Our objective was to use natural-abundance isotopes to distinguish between N_2O diffusion in pore water, N_2O production from NO_3^- via denitrification, and N_2O consumption via further reduction to N_2. Atmospheric N input into the peat bog was isotopically fingerprinted by monthly monitoring of wet deposition between January 2016 and May 2017. Runoff export was analyzed over the same period of time. Nitrate-N in runoff was isotopically heavier than NO_3^-N in atmospheric deposition (mean $\delta^{15}N$ values of -2.7‰ and -6.3 ‰, respectively), indicating export of secondary, organically cycled, residual nitrate. Nitrate-N in pore-water was identical to atmospheric deposition at a depth of 10-20 cm, isotopically very light at a depth of 30 cm ($\delta^{15}N$ of -9.5 ‰), and identical to runoff at a depth of 60 cm. Nitrous oxide concentrations in the atmosphere were nearly 20 % higher than in peat pore water gas, suggesting that the wetland served as a sink for air-borne N_2O, rather than a N_2O source. Within the vertical pore-water profile, nearly constant N_2O concentrations contrasted with a clear-cut shift towards higher $\delta^{15}N_{N2O}$ values up-core (from -5.0 to 2 ‰). In the 60-30 cm depth interval, there was a strong negative correlation between the $\delta^{15}N$ values of nitrate and nitrous oxide. Because reduction of NO_3^- to N_2O is associated with an isotope fractionation towards isotopically lighter N in the product, the found negative N isotope correlation explained denitrification process in this depth interval. We suggest that the relatively high $\delta^{15}N$ values of nitrate in the deepest peat layer reflected higher rates of NO_3^- reduction, compared to the

30-cm depth, and that the progressively heavier N_2O-N up-core corresponded to residual N_2O following partial reduction to N_2, along with an increasing proportion of atmospheric N_2O in the pore water.

6 Concluding remarks

1. Increased monsoon precipitation as predicted by global climate change scenarios for Southeast Asia in the future may even increase nitrate leaching from the Haean agricultural sub-catchment and seriously affect the quality of the Soyang lake drinking water reservoir. In order to avoid an increase of nitrate leaching from the Haean agricultural sub-catchment or better achieve reduced nitrate leaching a considerable reduction of nitrogen fertilizer application by local farmers is required. A specifically critical role in this framework is played by the dry land farming in the lower slopes of the Haean catchment. Regional decision makers are fully aware of this problem and initiated a change of agricultural practices. A switch from annual crop growing towards less fertilizer demanding and soil erosion preventing perennial crops, like ginseng, vineyards and orchards, is currently on the way (MAFRA, 2014, 2013; Yanggu Office, 2014).

2. Our results suggest that forest sub-catchments within the Soyang lake watershed in South Korea are under the influence of atmospheric nitrate deposition especially in periods of heavy monsoon rainfall. Although the main nitrate source in both forest river waters was microbial nitrification, the influence of wet atmospheric nitrate deposition played an important role especially in the mixed forest. The most probable reason for the lower nitrate retention capacity of the mixed forest is the lower nitrate assimilation capacity of conifers compared to broadleaf trees. Soil nitrate isotopes ($ð^{15}N_{NO3^-}$) along soil depth profiles showed gradients corresponding to what has been observed for soil total nitrogen $ð^{15}N$ by other studies (Nadelhoffer and Fry 1988; Gebauer and Schulze 1991; Gebauer et al. 1994; Högberg et al. 1996; Sah and Brumme 2003), but with an offset towards more negative $ð^{15}N$ values. The $ð^{15}N_{NO3^-}$ depth gradients of this investigation confirm for the first time under field conditions the conceptual model considerations by Nadelhoffer and Fry (1994) on the mechanisms and the isotope fractionation of microbial nitrogen mineralization and nitrification along depth gradients in forest soils.

3. Our study confirmed that the investigated ombrotrophic peat bog was not a major source of the greenhouse gas N_2O for the atmosphere. At the same time, N isotope systematics in the peat pore water indicated that denitrification proceeded, but probably at low rates and in deeper horizons along the peat profile. Only in depths 60-30 cm below surface a strong negative correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N\text{-}N_2O$ values was found as to be expected for denitrification with N_2O as end product. Low N_2O concentrations – sometimes even below N_2O concentration in the ambient atmosphere – accompanied by less negative or even positive $\delta^{15}N\text{-}N_2O$ values and a decoupling from the $\delta^{15}N\text{-}NO_3^-$ values indicate a further reduction of N_2O to N_2 in surface-near horizons of the peat profile.

7. Record of contributions to this thesis

Chapter 1

Chapter 1: Extended summary and synopsis were written by me. In this dissertation we present three manuscripts, two written by me and one was written by Martin Novak within collaboration between the Laboratory of Isotopes Biogeochemistry – University of Bayreuth and the Czech Geological Survey in Prague. All three manuscripts have been submitted. The contribution of me and all co-authors is listed below.

Chapter 2

Parra Suarez, S., Peiffer, S., Gebauer G. 2017. *Origin and fate of nitrate runoff in an agricultural catchment: Haean, South Korea – Comparison of two extremely different monsoon seasons* (submitted: Agriculture, Ecosystems and Environment, 05.12.2017; Submission N°: AGEE19540)

Parra, S.: 70% (concepts, field and laboratory work, interpretation, discussion and presentation of results, manuscript preparation)

Peiffer, S.: 10% (concepts, discussion of results)

Gebauer G: 20% (concepts, discussion of results, contribution to manuscript preparation)

Chapter 3

Parra Suarez , S., Gebauer, G. 2017. *The fate of monsoonal atmospheric nitrate deposition in two forest catchments in Soyang lake watershed, South Korea – A mass balance and stable isotope approach.* (Submitted: Biogeochemistry, 17.12.2017; Submission N°: BIOG-D-17-00332)

Parra, S.: 70% (concepts, field and laboratory work, interpretation, discussion and presentation of results, manuscript preparation)

Gebauer G: 30% (concepts, discussion of results, contribution to manuscript preparation)

Chapter 4

Novak, M., Parra Suarez, S., Gebauer, G., Thoma, M., Buzek, F., Cejkova, B., Jackova, I., Stepanova, M., Prechova, E., Curik, J., Veselovsky, F., Valkoca, I. 2017 Relationship between nitrogen isotope ratios of NO_3^- and N_2O in vertical porewater profiles through a polluted rain-fed peat bog (Ore Mts., Central Europe) (Submitted: Soil Biology and Biochemistry, 11.01.2018).

Novak, M: 25% (Concepts, results interpretation, manuscript preparation)

Parra-Suarez, S: 25% (Sampling design, field work, contribution to the manuscript preparation)

Gebauer, G: 15% (Concepts, supervision of the N_2O laboratory analysis)

Thoma, M: 10% (Field work)

Buzek, F: 10% (Nitrate laboratory analysis)

Cejkova, B: 2% (Laboratory work)

Jackova, I: 2% (Laboratory work)

Stepanova, M: 3% (Statistical analysis)

Prechova, E: 2% (Laboratory work)

Curik, J: 2% (Laboratory work)

Veselovsky, F: 2% (Laboratory work)

Valkova, I: 2% (Laboratory work)

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Chapter 2

Origin and fate of nitrate runoff in an agricultural catchment: Haean, South Korea – Comparison of two extremely different monsoon seasons

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Abstract

The monsoon season in South Korea has a great influence on the biogeochemical and hydrological processes in the entire country, but is specifically of concern in the Soyang lake watershed, the main drinking water reservoir for the 20 million metropolis Seoul. Therefore, control of water quality and especially nitrate concentrations in Lake Soyang is of high public priority. The Haean catchment is the most prominent agriculture-dominated sub-catchment of the Soyang lake watershed. It is a complex terrain influenced by extreme rain events and non-point nitrate sources. In this investigation we used: 1) a mass balance technique and 2) a $\delta^{15}N$ and $\delta^{18}O$ stable isotope approach to quantify and determinate the origin of nitrate inputs into the rivers that later flow into the lake. During pre-monsoon and monsoon seasons in 2013 and 2014 we measured daily rainfall and river water discharge at up to seven locations within a sub-catchment of the agricultural Haean catchment and collected rain, river water and groundwater samples in order to analyze nitrate concentrations and nitrate nitrogen and oxygen isotope abundances. Furthermore, we collected a wide range of nitrogen fertilizers as applied in the Haean catchment. Heavy monsoon events, as in 2013, were the most pronounced drivers of nitrate leaching being responsible for more than 80 % of the nitrate output in the river runoff. On the other hand, an almost missing summer monsoon in 2014 drove the nitrate runoff in a different manner, being responsible for only 0.4% of the total nitrate nitrogen river discharge in the previous year. Results of nitrate nitrogen and oxygen isotope abundance analyses suggest soil microbial nitrification as the most important contributor to the nitrate in the river runoff. In addition, nitrate from groundwater, specifically from the dry land areas, and partially affected by microbial denitrification contributed to the nitrate in the river runoff due to river-aquifer exchange fluxes especially after onset of the monsoon season. Direct leaching of nitrate from mineral fertilizers applied in the area and atmospheric nitrate deposition were obviously only minor contributors to the nitrate in the river runoff. Our investigation shows that in extremely different monsoon seasons, as in 2013 and 2014, the nitrate leaching in the Haean agricultural catchment was influenced by different hydrological and biogeochemical processes leading to different nitrate export scenarios during summer monsoon.

Keywords:

Nitrate, Monsoon, Stable isotope, Fertilizer, Groundwater, Aquifer.

1. Introduction

Nitrate leaching from agricultural land is considered as a hazardous source of pollution of surface water and groundwater systems (Zotarelli et al. 2007). Specifically, anthropogenic nitrogen fertilizer applications on agricultural land frequently lead to nitrate exports from rooted soil horizons to aquatic ecosystem like rivers, natural lakes and drinking water reservoirs. Nitrate export into aquatic systems causes eutrophication and acidification accompanied by deficiencies of dissolved oxygen and subsequent loss of animal and plant species (Camargo and Alonso 2007). Also drinking water with concentrations above 10 mg L^{-1} of N_{NO3}^- (Ward et al. 2005; World Health Organization 2011; Cheong et al. 2012; Kim et al. 2015) causes health problems of humans as the well-known methaemoglobinaemia or blue baby syndrome and also different types of cancer especially in the digestive tract (Powlson et al. 2008).

Soyang lake watershed in South Korea is the major drinking water reservoir for the 20 million metropolis Seoul. Therefore, control of water quality and especially nitrate concentrations in Lake Soyang is of high public priority. The identification of nitrate sources and total nitrate exports in the Soyang lake watershed is a major concern for decision makers in the entire country. The watershed has a complex terrain with different types of land uses, including patches of semi-natural silviculture and intensive agricultural management. In addition high altitudinal gradients and monsoon-driven extreme rainfall variations cause a high risk of nitrate leaching and soil erosion. These characteristics entail complex consequences and impacts in the environment that have to be considered for any improvement of water quality predictions in the region.

The Haean sub-catchment is the most prominent agriculture-dominated basin of the Soyang lake watershed. It is composed of a forested belt in the steep top slopes of the bowl-shaped basin, followed by a dry land agriculture belt in the bottom-slope areas and rice paddies at the bottom of the basin.

High nitrogen fertilizer application together with heavy monsoon rainfalls and sandy soils makes this basin a potential hazard in terms of nitrate losses. Heavy mineral nitrogen fertilizer applications are used to compensate for soil erosion loss. Adding sandy soil to the top layer of agricultural fields to compensate for soil loss is another common practice in Haean basin (Berger 2012). Thus a circle system difficult to break is created.

In areas with only one recognizable nitrate source the calculation of total nitrate exports might be sufficient for an effective decision making. However, in areas with complex terrain, extreme weather events and non-point nitrate sources, like in the Haean basin, a simple nitrate export mass balance would not be sufficient to elucidate in a mechanistic manner the origin of nitrate exports. Additional information on biogeochemical key processes in the nitrogen cycle is required.

Stable isotope natural abundance of nitrate is an ideally suited tool to add source and process information to nitrate mass balances on a catchment level.

Stable isotope abundance of nitrate has frequently been used for identification of nitrate origins. Unfortunately $\delta^{15}N_{NO3-}$ from different origins often shows overlapping ranges (Gormly and Spalding 1979; Kreitler 1979; Durka et al. 1994; Mayer et al. 2001, 2002; Koh et al. 2010). Therefore, additional measurement of $\delta^{18}O_{NO3-}$ allows a more precise classification of nitrate origins (Amberger and Schmidt 1987; Böttcher et al. 1990; Durka et al. 1994; Revesz et al. 1997; Aravena and Robertson 1998; Bräuer and Strauch 2000; Silva et al. 2000) particularly in agricultural areas where nitrate based fertilizers are used (Wassenaar 1995).

The use of solely $\delta^{15}N_{NO3-}$ for source identification is a valid technique as long as nitrate behaves conservative. Processes such as microbial nitrification or denitrification, however, are hard to be identified using only $\delta^{15}N_{NO3-}$ without additional support, since significant nitrogen fractionation occurs during these microbial processes (Wassenaar 1995) and their nitrogen isotope signatures have wide overlapping ranges (Mayer et al. 2001). On the other hand, during these microbial processes high fractionation affects simultaneously oxygen isotope abundance (Koh et al. 2010). For example nitrate produced during microbial nitrification contains two-thirds of its oxygen from soil water and one third of its oxygen from atmospheric oxygen (Andersson and Hooper 1983; Durka et al. 1994; Wassenaar 1995; Kendall 1998; Ohte et al. 2004). Thus, nitrate generated by microbial nitrification has distinct oxygen isotope ratios particularly different from atmospheric nitrate deposition, denitrification and fertilizers.

Another example is microbial denitrification, which causes enrichment in $\delta^{15}N$ and $\delta^{18}O$ in the remaining nitrate and simultaneously decreasing nitrate concentration (Mariotti et al. 1981, 1982). During denitrification $\delta^{15}N_{NO3-}$ increases about twice as fast as $\delta^{18}O_{NO3-}$ especially under closed system conditions (Melorose et al. 2015).

The dual isotope approach analyzing $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ is suited to separate nitrate that underwent nitrification and denitrification from each other and from other nitrate sources.

For example, Deutsch et al. (2006) successfully identify atmospheric deposition as one of three sources in a riverine zone. Einsiedl and Mayer (2006) identified proportional contributions of nitrate sources including nitrification, synthetic fertilizers and atmospheric deposition in groundwater in Germany.

In this study we come up with comparisons of nitrate export mass balances and underlying biogeochemical nitrate transformation processes in the Haean catchment for two years extremely different in their summer rainfall inputs. In 2013 a dry pre-monsoon season was followed by a monsoon season with rainfall amounts above the eleven-years average (Kim et al. 2007). In contrast, in 2014 a monsoon season almost completely failed leading to rainfall amounts clearly below the eleven-year average (Kim et al. 2007). We use the extreme differences in summer precipitation between 2013 and 2014 to develop scenarios for nitrate exports from agricultural catchments in summer monsoon climate regions under conditions as predicted by global climate change scenarios.

2. Materials and methods

2.1 Study site and land use

The field work of this research was conducted in the Haean-myun sub-catchment located in Yanggu–County, Gangwon Province, in the northeastern part of South Korea (128° 5' to 128° 11' E, 38° 13' to 38° 20' N). The punchbowl shaped basin is part of the Soyang lake watershed, which is the largest water reservoir in the country (Kim et al. 2000), and it is the main source of drinking water for the 20 million metropolis Seoul (Fig. 1). The Haean catchment has a total area of 64 km^2. It is the major farming territory of the entire watershed (Park et al. 2010) with about 30% area under agricultural land use (22% dry land fields and 8% rice paddies). 58% of the area are forested mountains and 12% are residential and semi-natural areas including grassland, field margins, riparian areas, channels, and farm roads (Arnhold et al. 2013). The topography of the area is complex with different hillslopes and flow directions (Arnhold et al. 2014). It has different altitudinal gradients characterized by flat areas and steep slopes in the mountain forested ridges (Park et al. 2010; Arnhold et al. 2014) The altitudinal elevation gradient reaches from 340 m above

sea level (asl) at Mandae River near the catchment outlet up to 1320 m asl in the surrounding mountain forests.

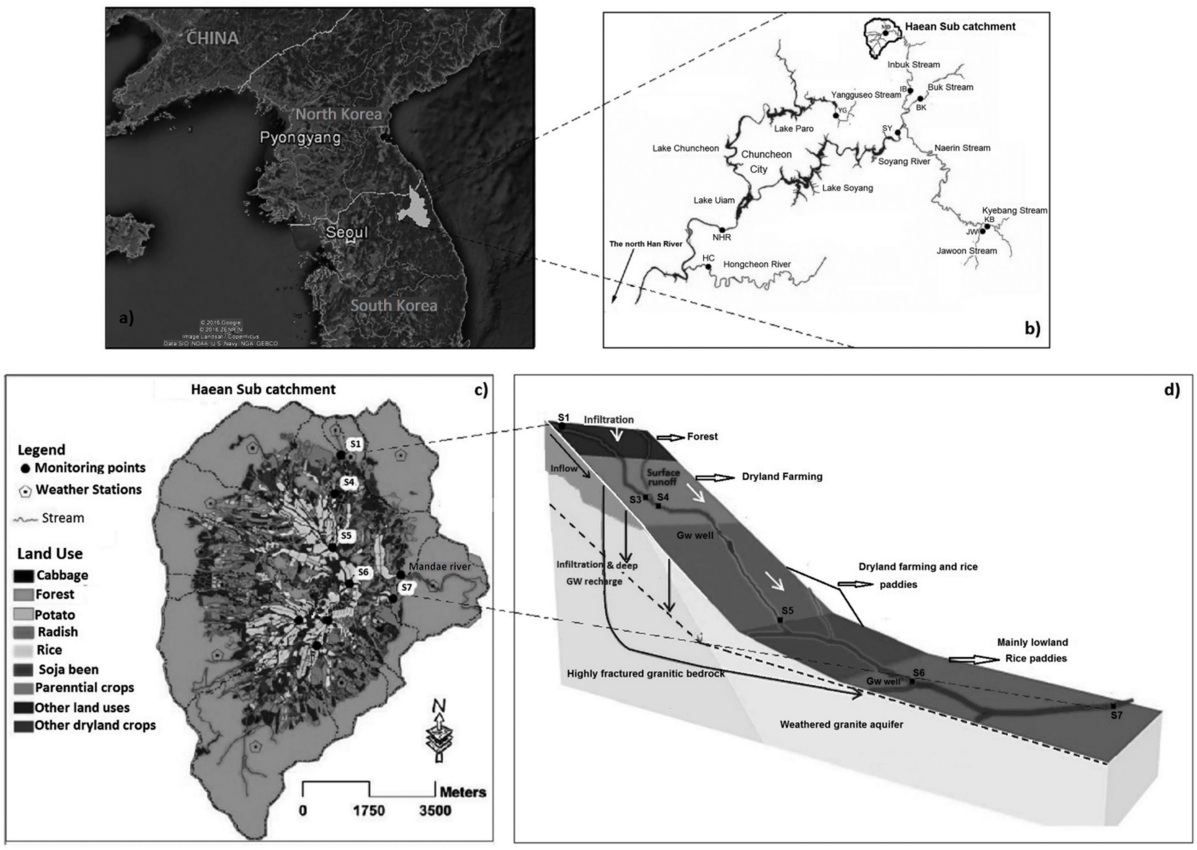

Fig. 1. Location of the Haean agricultural sub-catchment, (a) in the northeastern part of South Korea (b) within Soyang lake watershed. (c) Location of the sampling points in the sub-catchment of this investigation and (d) along an altitudinal gradient indicating positioning of the various land use systems and water flow pathways.

The maximum and minimum average temperatures in Haean basin per year span from –27˚C in winter to 33˚C in summer. The mean annual air temperature is 8.7˚C, and the annual precipitation based on 13 years weather station records in the Haean catchment is 1658 mm, (Maharjan 2015). Almost 90% of the annual precipitation occurs within the cropping season from April to October (Kettering et al. 2012). The monsoon season has place in July, August, and September and it has a great influence on the biogeochemical and hydrological processes as it represents more than 65% of the precipitation concentrated just in this period (Arnhold et al. 2013). This heavy rain contributes with significant non-point pollution nutrients to the water systems (Kim 2006) that eventually will feed into Lake Soyang.

Monsoon season has defined periods, a dry pre-monsoon period placed between April until end of June and a monsoon period which follows between July until beginning of September. It should be mentioned that due to the influence of climate change and other variables these periods can fluctuate or even not appear. The sampling campaign in 2013 went from May (mid dry pre-monsoon period) until mid August when the intensive and median precipitation events have evidently stopped and the monsoon season have reached an end. In 2014 the sampling collection started about a month later than the year before, because during dry pre-monsoon period in 2013 the lack of rain did not allow us to collect enough water to be analyzed. In 2014 a monsoon almost completely failed.

For our research, a sub-catchment within the basin was chosen as the most representative in terms of land use and water flow (Fig. 1d). An altitude gradient with different land use patches along the stream started with steep slopes in a forested land located in the higher part of the river, followed by dry land crops on a lower elevation and predominately rice paddies located downstream in the lowest part of the valley (Fig.1d). The forest vegetation patch is deciduous and represents with 13.25 ha 0.4% of the whole forested area in the catchment. It is dominated by *Quercus dentata*, *Q. mongolica*, *Q. serrata*, *Betula davurica*, and *Tilia amurensis* as major tree species, but also in a minor proportion, *Weigela florida*, *Stephanadra incisa*, *Ulmus laciniata*, *Symplocos chinensis*, *Euonymus alatus*, *Acer pseudosieboldianum*, and *Corylus heterophylla* (Berger 2012). The main dry land crops cultivated in Haean catchment were in the years of the investigation primarily cabbage, potato, radish and soybean (7.8 %), orchards and ginseng (8.3 %), and maize, pepper, rye, and sunflowers (4.1 % of the total catchment included as other dryland crop) (Maharjan 2015). The dry land patches represent with 144 ha 10.3% of the total dry land area in the basin. The rice field area is with 42 ha 8% of the total rice paddies in Haean catchment. In total the sub-catchment area surrounding the sampling and monitoring points is with 200.7 ha 3.13% of the total Haean area.

2.2 Field instrumentation and data collection

Six monitoring and sampling points were located along the stream channel starting in the upper forest patch S1. In the middle of this altitudinal gradient and located in the dry land patch is S2, S3 and S4, while S5 and S6 were located in the lower rice paddies patch (Fig. 4). During the campaign in 2014, water samples from the dry land patch were collected only from S2 and S4 because no major differences were found between S2 and S3 in the year before.

2.2.1 Weir locations and discharge calculations

River discharge was measured with two V-notch weirs located in S1 (forest patch) and S3 (dry land patch) for high and low flows (Ackers et al. 1978; Chanson and Wang 2012, 2013). Water level and barometric data used in discharge calculations were measured at the weir with absolute pressure transducers which recorded total head at 5 min intervals (Levelogger® Edge Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada) and barologgers (Barologger Edge Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada) for barometric compensation. For low and moderate flows (<8.0 $m^3. s^{-1}$) the flow velocities were measured with an electromagnetic current meter (FlowSens, ±0.5%, SEBA Hydrometrie GmbH, Kaufbeuren, Germany) in S4, S5 and S6 monitoring points.

V-notch weir discharge values were calculated using the Kindsvater and Shen formula (Kulin and Compton 1975; El-Ansary et al. 2010) while the velocity-area method was applied for the low and moderate flows using the electromagnetic device (Herschy 1985; Peters 1988).

2.2.2 Weather stations and rainfall measurements.

Precipitation was recorded in 5 min intervals using an automatic weather station (WS-GP1, Delta-T Devices, Cambridge, UK). Two weather stations were located in S1 (higher forested patch) and S6 (lower rice paddies patch). Rainfall collectors were also located in S1, S4 and S6 monitoring points.

2.2.3 Groundwater wells

Groundwater wells were installed perpendicular to the stream at different elevation zones of the altitudinal transect. The first transect wells were located in the middle elevation area S4 (dry land patch). They consisted of two 2-inch diameter, polyvinyl chloride (PVC) piezometers with 0.5 m screened intervals at their lower end. Depths of the piezometers were 4.00 and 6.00 meter respectively. The second transect wells were installed at the lower elevation area S6 (rice paddies patch). They consisted of four wells with the same characteristics of the first transect wells and with depths of 6.00, 5.00, 4.00 and 3.00 m. All wells were equipped with absolute pressure transducers (Levelogger, Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada, ±0.01 m), which recorded total head in 5 min intervals. Water level readings recorded by level loggers were corrected for atmospheric pressure variations by using the atmospheric pressure readings of a Barologger (Barologger, Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada), attached outside of the wells.

2.3 Sample collection, storage, transportation and analysis.

The sampling design was made to determinate the influence of the precipitation regime and land use on the sources and total nitrate discharge into Mandae River, one of the most important streams in Soyang lake watershed. Stream, rain and groundwater samples were collected for nitrate concentration and nitrate stable isotope abundance analysis.

During the field campaign, samples were collected every second day and after every rain event in the dry pre-monsoon season. During heavy monsoon season samples were collected after rain events and up to every six hours in precipitation events that lasted at least 12 hours.

All samples were taken manually and stored in 1 L plastic bottles for nitrate isotope abundance and 2 ml vials for nitrate concentration analysis. Precipitation samples were collected from the rain collectors installed at S1, S4, S6 monitoring points. The rain collectors were installed in open areas at 1.50 m above the ground.

Groundwater samples were collected only during growing season 2013 as nitrate concentrations within the wells behave conservative. Groundwater samples were collected from each of the wells using a submersible pump (Power Jet High Pressure pump 22 L. min^{-1} Tauchpumpe REICH GmbH, Eschenburg, Germany).

After collected, the water samples were immediately frozen and stored for their subsequent transport to Germany for further analysis. In aim to keep the samples frozen during the transportation, dry ice was added to the cooling boxes. In 2013 we collected 175 rain samples, 300 river water samples and 288 groundwater samples for nitrate concentrations. For isotope abundance analysis we collected 50 river water samples and 30 groundwater samples. To complete the sampling collection during 2014 we collected 110 rain samples and 210 river water samples for nitrate concentration analysis. For isotope abundance analysis we collected 47 river water samples.

In addition to the water samples the following in the Haean sub-catchment commonly used nitrogen fertilizers were collected for the subsequent nitrogen and oxygen isotope abundance analysis. We collected in total 13 fertilizer samples including manure, vegetable compost, organic fertilizer 15% animal waste, KNP fertilizer, NK fertilizer and N fertilizer 70% nitrate.

Analysis of nitrate concentration and nitrate isotope abundance were completed at the Hydrology Department and Isotope Biogeochemistry Laboratory of Bayreuth University, respectively.

2.3.1 Nitrate concentration analysis.

Rain, stream and groundwater samples were analyzed for nitrate concentration using anion exchange high performance liquid chromatography and subsequent UV detection (HPLC LC4000 Jasco Europe S.r.l., Cremella, Italy) using PeakSimple Chromatography software (PeakSimple 3.93) and an anion exchange IC column (VYDAC 302IC 10 µm Anion Exchange 250 x 4.6mm, Grace Corporate Headquarters, Columbia, USA). For further details of this method see Gebauer et al. (1984). The samples were unfrozen inside of a refrigerator at 4^{o}C 12 hours before the analysis.

2.3.2 Sample preparation and nitrate isotope abundance analysis.

The nitrate extraction from the water samples for the subsequent isotope abundance analysis followed the procedure described by Huber et al. (2011) and consisted of the following steps:

(1) Unfreezing of the 1 L stream and groundwater samples in a refrigerator at 4° C for 24 h. Transferring the water samples into glass vessels, freezing the samples at -40°C in a salt/ethanol bath and complete freeze-drying of the samples. Due to the high number of samples and their high volume, the following freeze-drying machines were used in parallel: Freeze Dryer condenser EF4 Modulyo with two levels of 12 port acrylic lid, Edwards High vacuum B.O.C. Ltd, Crawley, England and SuperModulyo freeze dryer 20 L with Column manifolds 24 port, Edwards High vacuum B.O.C. Ltd, Crawley, England.

(2) Extraction of nitrate in a NaI + acetone + hexane solution, settling of insoluble compounds overnight in a refrigerator and subsequent centrifugation (Beckmann J6 High Capacity Centrifuge, Beckmann Coulter, Krefeld, Germany). Transfer of the supernatant into new centrifugation tubes and precipitation of $Ba(NO_3)_2$ by adding of BaI_2 in acetone. After settling of the precipitate in a refrigerator and centrifugation, decantation of the supernatant and drying of the $Ba(NO_3)_2$ at 60°C overnight. Dissolving of the $Ba(NO_3)_2$ in defined water volumes and transfer of aliquots into tin (for N isotope abundance analysis) or silver capsules (for O isotope abundance analysis) and again complete drying of the samples before closure of the capsules.

Relative nitrogen isotope abundances of the nitrate samples ($\delta^{15}N_{NO3}^-$) were measured with an elemental analyzer (Carlo Erba 1108, Milano, Italy) for Dumas combustion followed by gas chromatography and feeding of N_2 into a continuous flow isotope ratio mass spectrometer (delta S Finnigan MAT, Bremen, Germany) via a ConFlo III interface (Thermo Fisher Scientific, Bremen, Germany) as described by Bidartondo et al. (2004). Nitrogen standard gas was calibrated with respect to the international standard (N_2 in air) by using the reference substances N1 and N2 provided by the IAEA (International Atomic Energy Agency, Vienna, Austria). Nitrogen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard acetanilide with known nitrogen content of 10.36% (Gebauer and Schulze 1991). For recovery control of our extraction procedure nitrogen amounts in a randomly selected sample subset were compared to the independently by HPLC measured nitrate concentrations. Nitrogen recovery was always close to 100%.

Relative oxygen isotope abundances of the nitrate samples ($\delta^{18}O_{NO3}^-$) were measured by thermal conversion through pyrolysis (HTO, HEKAtech, Wegberg, Germany) followed by gas chromatography and feeding of CO into a continuous flow isotope ratio mass spectrometer (delta V advantage Thermo Fisher Scientific) via a ConFlo IV interface (Thermo Fisher Scientific) as described by Gebauer et al. (2016). The CO standard gas was calibrated with respect to the international standard (V-SMOW) by using the reference substances IAEA601 and IAEA602 provided by the IAEA. Oxygen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard benzoic acid with known oxygen content of 26.20%. For recovery control of our extraction procedure oxygen amounts in a randomly selected sample subset were compared to the independently by HPLC measured nitrate concentrations. Oxygen recovery was close to 100% for the nitrate extracted from water collected in 2013. However, for the nitrate extracted separately from water collected in 2014 oxygen recovery exceeded the 100% threshold significantly. Thus, for the 2014 samples the isolated nitrate was obviously still contaminated with other oxygen-containing compounds for unknown reasons. Thus, all $\delta^{18}O_{NO3}^-$ data of the 2014 sample collection were not considered for any further data presentation.

In addition to $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ of water samples we also analyzed $\delta^{15}N$ and $\delta^{18}O$ of nitrogen fertilizer samples using the above described equipment.

2.4 Calculation of nitrate fluxes, isotope data treatments and statistical analyses

Nitrate-N flux calculations in the river discharge were carried out using N_{NO3}^- concentrations calculated from measured nitrate concentrations and multiplied by the total stream area discharge or rain input per day. Proportional N_{NO3}^- input from rainfall was calculated based on the average mineral fertilizer N applications during the growing season in Haean (313 kg N ha-1 yr-1) (Kim et al. 2008).

Nitrate stable isotopes data from stream and groundwater samples were plotted together with the natural abundance known for the major nitrate sources that may influence aquifers (Kendall 1998) as nitrate from microbial nitrification and denitrification.

A theoretical $\delta^{15}N_{NO3-}$ /$\delta^{18}O_{NO3-}$ relationship for microbial nitrification was calculated to compare nitrate originating from microbial nitrification with the measured stream and groundwater nitrate isotope abundance data in the research area. Nitrate from microbial nitrification of soil organic nitrogen has two thirds of its oxygen from soil water (-13.5 $^0/_{00}$ and -5.5 $^0/_{00}$, OIPC; Bowen, 2008; Bowen et al., 2005) and one third from atmospheric 0_2 (~+23.5 $^0/_{00}$). Thus we can calculate the theoretical $\delta^{18}O_{NO3-}$ of nitrate of microbial nitrification for the Haean agricultural sub- catchment by using the following equation:

$$\delta^{18}O_{NO3-} = {}^2/_3\,(\delta^{18}O_{-H2O}) + {}^1/_3\,(\delta^{18}O_{-O2}).$$

Also microbial denitrification is associated with a systematic shift in the isotopic composition of the remaining nitrate in a relationship **2** $(\delta^{15}N)$**: 1**$(\delta^{18}O)$ (Amberger and Schmidt 1987; Böttcher et al. 1990; Kendall 1998). In this way nitrate that underwent denitrification can be distinguished from nitrate that was simply diluted. Nitrate that underwent denitrification is characterized by a shift of $\delta^{15}N$ and $\delta^{18}O$ towards more positive values (Aravena and Robertson 1998). Also $\delta^{15}N$ and $\delta^{18}O$ values of inorganic fertilizers and manure used in the research area were plotted together with river and groundwater samples. Stable isotope composition of atmospheric rain deposition was obtained from Lee et al., (2008).

We also used a linear regression analysis between $\delta^{15}N_{NO3-}$ and In N_{NO3-} (inverse natural logarithm of the nitrate-N concentrations) in river water. This analysis provides information on the occurrence of microbial denitrification (Mariotti et al. 1988) without the need of $\delta^{18}O_{NO3-}$ data, which were not

available for the 2014 water collection. Significant differences were analyzed using a Mann–Whitney U-test, a highly efficient nonparametric test.

Statistical analysis and graphs were carried out using the statistical software package SigmaPlot (Version 11, Systat Software, Erkrath, Germany). A simple linear fitting regression with significance level of $P \leq 0.05$ was run in the program for all isotope data. Correlation analyses were run between nitrate concentration and river discharge or rainfall data.

3. Results

3.1 Hydrological characteristics

Extremely different weather conditions characterized the growing seasons in 2013 and 2014. Precipitation events differed considerable between years. While heavy rain monsoon season in 2013 was extremely wet (706.9 mm), during summer 2014 it was greatly dry and the rain events were scarce without a clear presence of a monsoon season (172 mm). The total rain in the growing season of 2014 was only 24% of the total precipitation in the year before. Two marked periods were observed during the sampling campaign in summer 2013. A dry pre-monsoon season, measured from mid-May to end of June with precipitations that ranged from 0.2 to 33.2 mm d^{-1} and a wet monsoon season from July to August, with storm events ranging from 1.2 to 92.4 mm d^{-1} (Table 1a). The strongest storm event was recorded on July 8th. This event lasted 20 hours and had an intensity ranging from 2 to 48.9 mm h^{-1}. The year 2014 was generally dry, without a clear monsoon season. Precipitations in this year ranged from 0.2 to 14.2 mm d^{-1} during June and from 0.2 to 63 mm d^{-1} in July and August (Table 1a). Although 2014 was a dry year, we assumed that the scarce rain events during July and August were part of the monsoon season. The strongest storm event in 2014 was recorded on July 25th.This event was intermittent and lasted about 9 hours throughout the day. Its biggest intensity was 21.6 mm h^{-1}. Only two rain events were moderately strong during July and August 2014 (Fig. 2b).

Table 1. Maximum (Max), minimum (Min) and average (Ave) daily (a) input (mm d^{-1}) and (b) discharge runoff (m^3 d^{-1}) data for the investigated Haean agricultural sub-catchment during the sampling campaigns in 2013 and 2014. On days without rainfall the minimum of daily input was of course zero. Daily values were summed up to obtain total rain input (mm) and discharge runoff (m^3) data and separated for the usually dry pre-monsoon season (May and June) and the usually rainy monsoon season (July and August).

Haean agricultural sub-catchment		**2013**		**2014**	
Hydrological characteristics		***Pre-monsoon season***	***Monsoon season***	***Pre-monsoon season***	***Monsoon season***
(a)	**Max (mm d^{-1})**	33.2	92.4	14.2	63
Rain	**Ave (mm d^{-1})**	10.2±9.0	28.1±25.1	4.4±4.1	13.1±20.2
	Min (mm d^{-1})	0.2	1.2	0.2	0.2
	Total (mm)	144.1	562.8	41.6	131.6
(b)	**Max (m^3 d^{-1})**	$7.3x10^3$	$11.1x10^5$	226.06	898.44
Discharge	**Ave (m^3 d^{-1})**	$554.8±1.0x10^3$	$92.3x10^3±1.7x10^5$	17.6	140.2
	Min (m^3 d^{-1})	0.4	0.2	0.1	0.1
	Total (m^3)	$37.3x10^3$	$49.6x10^5$	$1.5x10^3$	$1.2x10^3$

The discharge during pre-monsoon season in June 2013 was similar along the stream without major changes between sampling points. It ranged from 0.4 to 7.3 x10^3 m^3 d^{-1} (Table 1b). During monsoon season the discharge along the stream was different between sampling points, mainly due to the changes in the dimensions of the riparian zone and the increase of surface runoff. The average in the discharge upstream was around 5.9 x 10^3 m^3 d^{-1} and the average in discharge downstream was around 84.0 x 10^3 m^3 d^{-1}. Total discharge during monsoon season ranged from 0.2 to 11.1 x 10^5 m^3 d^{-1} (Table 1b). In 2014 discharge was very low due to the lack of rain. In June no major changes were measured along the stream. In this month discharge ranged from 0.1 to 226.06 m^3 d^{-1} while in July and August discharge had values from 0.1 to 898.44 m^3 d^{-1} (Table 1b).

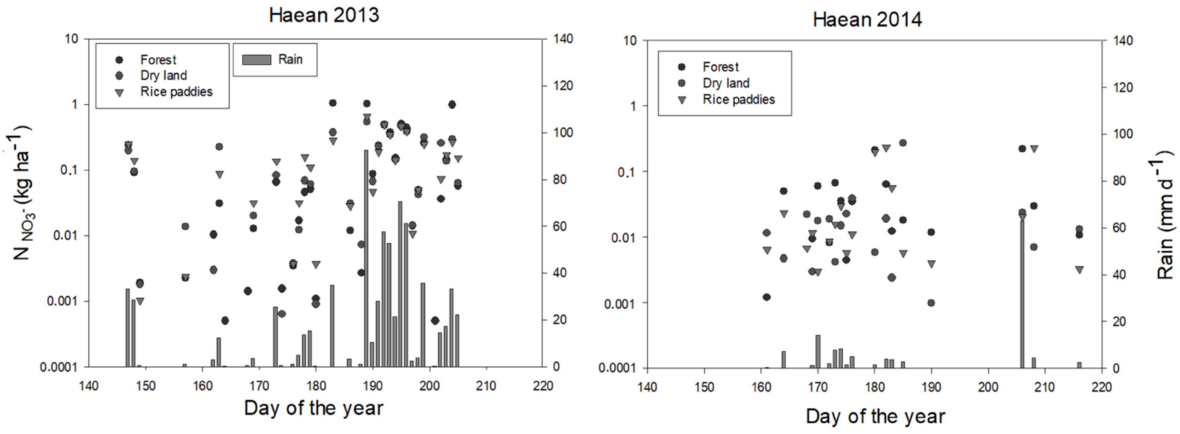

Fig. 2. Nitrogen input from nitrate deposition by rainfall (kg ha^{-1}) measured at the three sampling locations forest, dry land and rice paddies within the investigated Haean agricultural sub-catchment and temporal distribution and intensity of rainfall events during the sampling campaigns (May to August) 2013 and 2014.

3.2 Nitrate concentrations and seasonality of nitrate fluxes

3.2.1 Rainfall

In the growing season of 2013 and 2014 nitrate concentrations in rainfall ranged between 0.6 or 0.2 and 16.9 or 13.6 mg L^{-1} respectively. These most extreme concentrations were always found in the pre-monsoon season (Table 2). Mean nitrate concentrations in rainfall were quite similar for pre-monsoon and monsoon season and for the years 2013 and 2014 and ranged between 2.4 and 3.8 mg L^{-1} (Table 2). However due to different rainfall, nitrogen input from nitrate in rainfall over the sampling periods from May to August was on an area basis in 2013 much higher (16.4 kg N_{NO3-} ha^{-1}) than in 2014 (2.1 kg N_{NO3-} ha^{-1}). The forest area received in both years more N_{NO3-} ha^{-1} and higher

proportional N_{NO3-} than the agricultural areas (Table 3). Figure 2 provides an overview over the temporal distribution of rainfall and N_{NO3-} input per area unit. No significant correlations between rainfall and NO_3^- concentrations in precipitation were found in any of the years ($p>0.050$). The N_{NO3}^- input by rainfall during the monsoon season in 2013 was 9% of the total river N_{NO3}^- discharge. In 2014 the N_{NO3}^- river discharge was lower than the total N_{NO3}^- rain input (Tables 3 and 5). Related to the mineral nitrogen fertilizer application rate common in Haean (313 kg N ha^{-1} yr^{-1}) nitrogen input from nitrate rain deposition was only 5.2% in 2013 and 0.7% in 2014.

Table 2. Maximum (Max), minimum (Min) and average (Ave) nitrate concentrations (mg L^{-1}) in rainfall in the investigated Haean agricultural sub-catchment during the sampling campaigns in 2013 and 2014. Nitrate concentrations are separated for the usually dry pre-monsoon season (May and June) and the usually rainy monsoon season (July and August).

Haean agricultural sub-catchment		**2013**		**2014**	
Nitrate concentrations		**Pre-monsoon season**	**Monsoon season**	**Pre-monsoon season**	**Monsoon season**
Rain	**Max (mg L^{-1})**	16.9	13.2	13.6	9.2
	Ave (mg L^{-1})	2.8±2.5	3.8±2.1	2.4±2.5	2.8±2.2
	Min (mg L^{-1})	0.6	1.0	0.2	0.9

Table 3. Total nitrogen input from nitrate deposition by rainfall separated for three sampling areas, forest, dry land and rice paddies and for the campaigns in 2013 and 2014 and calculated on a hectare basis (kg N_{NO3-} ha $^{-1}$), on a percentage basis or on the basis of the area covered by the three respective sampling regions (kg N_{NO3-} area $^{-1}$) in the investigated Haean agricultural sub-catchment.

Haean agricultural sub-catchment		**2013**			**2014**		
Sampling plot land use	***ha***	***N_{NO3-} kg ha^{-1}***	***N_{NO3-} kg Area^{-1}***	***Percentage (%)***	***N_{NO3-} kg ha^{-1}***	***N_{NO3-} kg Area^{-1}***	***Percentage (%)***
Forest area	13.2	6.4	85.9	39.3	1.4	18.4	63.5
Dry land area	144.8	5.0	725.7	30.4	0.6	160.2	30.0
Rice paddies area	42.6	4.9	212.4	30.2	0.1	37.2	6.4
Total	200.7	16.4	1024.1	100	2.1	162	100

3.2.2 Stream runoff

Nitrate concentrations in river discharge ranged between 0.4 mg L^{-1} and 64.1 mg L^{-1} in 2013 and between 1.2 and 27.6 mg L^{-1} in 2014. Extreme nitrate concentration values of 34.5 and 64.1 mg L^{-1} were found during the dry pre-monsoon season in 2013 at the rice paddies patch and during the monsoon season at the dry land patch respectively (Fig. 3 and Table 4). In 2013 mean nitrate concentrations in stream runoff from the forested site (S1) ranged in the order of about 10 mg L^{-1} and thus, was about half of the mean nitrate concentrations measured in the stream runoff from the dry land (S2, S3 and S4) and rice paddy (S5 and S6) patches (Table 4). In the monsoon season of the wet year 2013 mean nitrate concentrations in stream runoff from the forest, dry land and rice paddy patches were always slightly lower than in the pre-monsoon season (Table 4). Maximum, minimum and average nitrate concentrations in stream runoff in the dry year 2014 were almost consistently lower than in 2013 and no systematic differences between pre-monsoon season and monsoon season were found (Table 4, Fig. 3). In 2014 again, the average nitrate concentrations in the stream runoff from the forest were considerably lower than in the stream runoff after passage of the dry land and rice paddies. No significant relationship between discharge and nitrate concentrations in river water was found in any of the years ($p>0.050$).

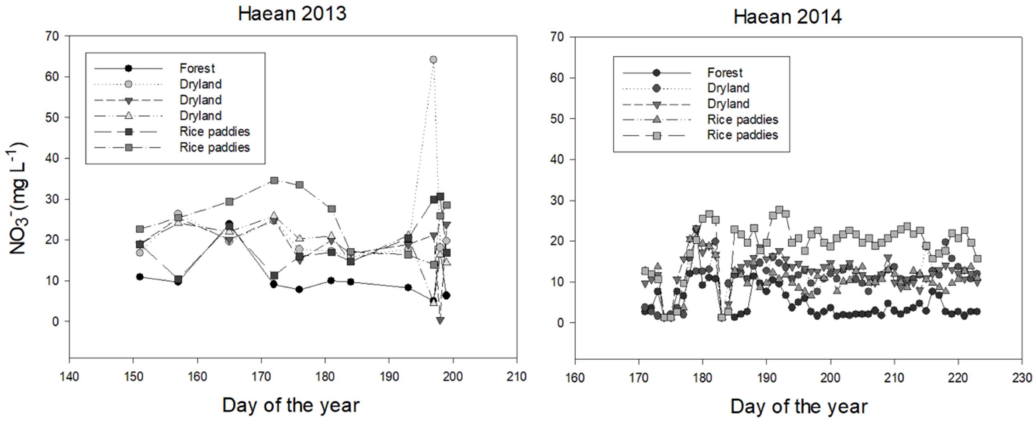

Fig.3. Temporal distribution of nitrate concentrations (mg L^{-1}) in stream runoff measured at the three sampling locations forest, dry land and rice paddies within the investigated Haean agricultural sub-catchment during the sampling campaigns (May to August) in 2013 and 2014. During sampling campaign 2013 values from S2, S3 and S4 within dry land were considered for this graph, while during sampling campaign 2014 only the values from S2 and S4 were considered due to the lack of differences between S2 and S3 in the year before.

Table 4. Maximum (Max), minimum (Min) and average (Ave) nitrate concentrations (mg L^{-1}) in stream runoff measured at the three sampling areas forest, dry land and rice paddies within the investigated Haean agricultural sub-catchment during the pre-monsoon (May and June) and monsoon season (July and August) of the sampling campaigns in 2013 and 2014. Dry land data was calculated from three sampling points (S2, S3 and S4) in 2013 and from two sampling points (S2 and S4) in 2014.

Nitrate concentrations		***Pre-monsoon season 2013***			***Monsoon season 2013***			***Pre-monsoon season 2014***			***Monsoon season 2014***		
Sampling point		***Forest (S1)***	***Dry land (S2,S3 and S4)***	***Rice paddies (S5 and S6)***	***Forest (S1)***	***Dry land (S2,S3 and S4)***	***Rice paddies (S5 and S6)***	***Forest (S1)***	***Dry land (S2 and S4)***	***Rice paddies (S5 and S6)***	***Forest (S1)***	***Dry land (S2 and S4***	***Rice paddies (S5 and S6)***
Stream	**Max (mg L^{-1})**	23.8	26.4	34.5	18.1	64.1	30.6	22.8	23.1	26.6	11.3	19.7	27.6
	Ave (mg L^{-1})	12.2±5.6	20.9±3.4	22.5±7.6	9.5±2.4	17.1±6.8	20.6±5.8	7.7±5.6	9.6±6.8	12.0±7.9	4.0±2.8	12.3±3.1	15.2±6.1
	Min (mg L^{-1})	7.7	15.0	10.3	5.0	0.4	13.9	1.2	1.2	1.2	1.2	1.2	1.2

Total N_{NO3}^- river discharge fluxes measured at four sampling locations are represented in Fig. 4 in a multiple line and scatter flux diagram over time and in Table 5 calculated as cumulative values. Rather striking is the difference in total NNO3- river discharge between the sampling periods in 2013 and 2014. While total NNO3- river discharge in the growing season of 2013 was 10.3 x 10^3 kg for the entire sub-catchment area, it was 43.4 kg for the entire sub-catchment area in 2014, which represents just 0.4% of the total N_{NO3}^- river discharge in 2013. This huge difference was mainly driven by the pronounced N_{NO3}^- river discharge fluxes during the heavy monsoon season in 2013 (Fig. 4). The N_{NO3}^- river discharge increased with the frequency of rainfall during the monsoon season in 2013. This period contributed 90% to the total N_{NO3}^-discharge during the whole sampling campaign in 2013. The N_{NO3}^- river discharge in the pre-monsoon season and the weak monsoon season in 2014 showed no such difference. Dry land field patches contributed more than 60% to the entire total N_{NO3}^- river discharge in the growing season of 2013, while the rice paddy patch contributed about 25% and the forest patch only 13% (Table 5). In 2014 the proportional contribution to the total N_{NO3}^- river discharge was highest for the rice paddy patches.

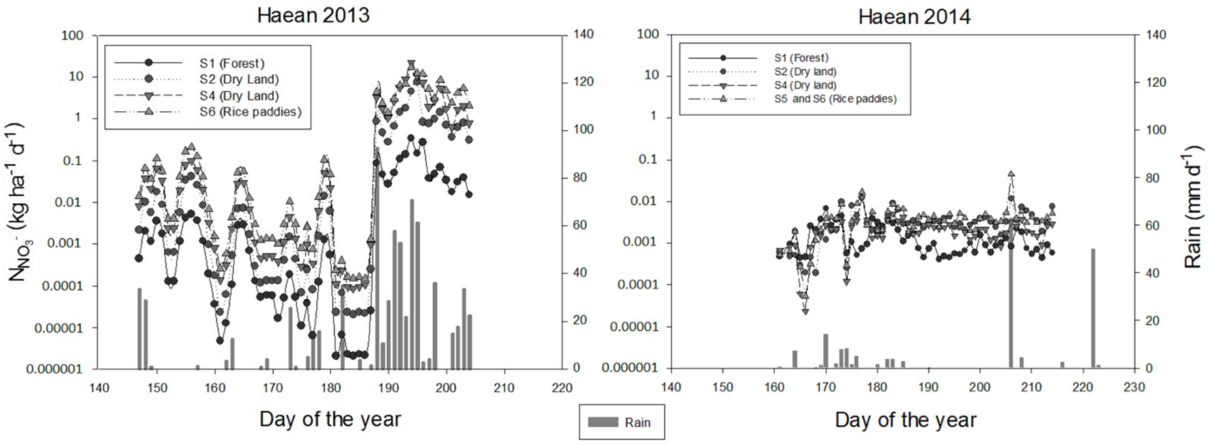

Fig. 4. Temporal distribution of total N_{NO3-} fluxes (kg ha^{-1} $d^{-1)}$ in stream runoff measured at three sampling locations forest, dry land and rice paddies within the investigated Haean agricultural sub-catchment during the sampling campaigns (May to August) in 2013 and 2014. One single value for rice paddies is given in this graph because the areas of S5 and S6 were measured together within a total rice paddies area. The value of N_{NO3-} fluxes (kg ha^{-1} d^{-1}) is calculated with the mean nitrate concentration values between S5 and S6 in both years.

Table 5. Total nitrogen discharge runoff separated for three sampling areas, forest, dry land and rice paddies and for the campaign in 2013 and 2014 and calculated on a hectare basis (kg N_{NO3-} ha $^{-1}$) on a percentage basis or on the basis of the area covered by the three respective sampling regions (kg N_{NO3-} area $^{-1}$) in the investigated Haean agricultural sub-catchment. One single value for rice paddies is given in this graph because the areas of S5 and S6 were measured together within a total rice paddies area. The value of N_{NO3-} fluxes (kg ha^{-1} d^{-1}) is calculated with the mean nitrate concentration values between S5 and S6 in both years.

Haean agricultural sub-catchment		**2013**			**2014**		
Sampling plot land use	***ha***	***N_{NO3-} kg ha^{-1}***	***N_{NO3-} kg area^{-1}***	***Percentage (%)***	***N_{NO3-} kg ha^{-1}***	***N_{NO3-} kg area^{-1}***	***Percentage (%)***
Forest	13.2	23.5	312.6	13.0	0.08	1.05	9.0
Dry land S2	61.3	56.2	$3.4x10^3$	31.1	0.19	11.4	21.2
Dry land S4	83.5	56.0	$4.7x10^3$	31.0	0.12	9.9	13.5
Rice paddies	42.6	44.7	$1.9x10^3$	24.7	0.49	21.0	56.1
Total	200.72		$10.3x10^3$	100		43.49	100

3.2.3 Groundwater

Nitrate concentration in groundwater ranged between 0.2 and 67.0 mg L^{-1}. Extreme values of 67 and 65.7 mg L^{-1} were recorded at the rice paddies in the beginning of the pre-monsoon season and the end of the monsoon season (Fig. 5 and Table 6). A pronounced difference between nitrate concentration in groundwater at the dry land field and rice paddy patches was found (Fig. 5). In dry land field groundwater nitrate concentrations ranged from 0.2 to 39.4 mg L^{-1} while groundwater nitrate concentrations at the rice paddies ranged from 18.0 to 67.0 mg L^{-1} (Table 6). Pronounced differences in groundwater nitrate concentrations between dry pre-monsoon season and monsoon season were not found in any of the sites. We found significant differences ($p<0.001$) between the wells sampled within the dry land (Fig 5 well 1 and well 2). Significant differences in nitrate concentrations were found between groundwater at dry land field patches and rice paddy patches ($p< 0.001$). The high groundwater nitrate concentrations specifically in the rice paddy area but also in some parts of the dry land area suggested an impact of nitrogen fertilizer application on groundwater quality.

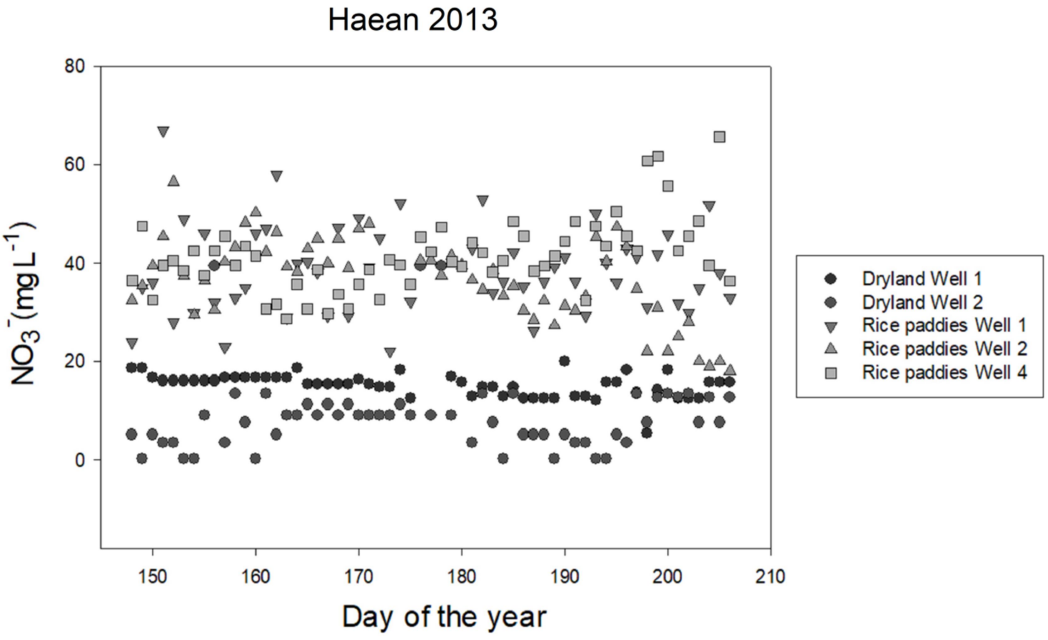

Fig. 5. Temporal distribution of nitrate concentrations (mg L^{-1}) in groundwater measured at two sampling locations dry land (two wells) and rice paddies (three wells) within the investigated Haean agricultural sub-catchment during the sampling campaigns (May to August) in 2013.

Table 6. Maximum (Max), minimum (Min) and average (Ave) nitrate concentrations (mg L-1) in groundwater measured at two sampling locations dry land (two wells) and rice paddies (three wells) within the investigated Haean agricultural sub-catchment during the sampling campaigns (May to August) in 2013.

Haean agricultural sub-catchment		**2013**				
Nitrate concentrations		***Pre-monsoon season***		***Monsoon season***		
Sampling point		***Dry land (S4)***	***Rice paddies (S6)***	***Dry land (S4)***	***Rice paddies (S6)***	***All wells***
Groundwater	**Max (mg.L^{-1})**	39.4	67.0	20.0	65.7	67.0
	Ave (mg.L^{-1})	13.5±8.3	39.3±7.5	10.6±5	38.1±9.5	28.0±15.3
	Min (mg.L^{-1})	0.2	22.1	0.3	18.0	0.3

3.3 Stable isotope abundances in nitrate and fertilizers.

Nitrate $\delta^{15}N$ and $\delta^{18}O$ values in atmospheric input (rain), stream water and groundwater and $\delta^{15}N$ and $\delta^{18}O$ values in mineral and organic fertilizers are summarized in the Table 7. Mineral fertilizers applied in the study area have nitrate $\delta^{15}N$ values ranging between 0.6 $^{0}/_{00}$ and 2.7 $^{0}/_{00}$. Nitrate $\delta^{18}O$ values in mineral fertilizers were ranging between 20.4 and 40.5 $^{0}/_{00}$. In comparison to mineral fertilizers, organic fertilizers were found to be enriched in ^{15}N with $\delta^{15}N$ between 3.4 and 9.6 $^{0}/_{00}$ and depleted in ^{18}O with δ^{18} between 3.5 and 15.1 ‰. Based on literature data the nitrate input by rainfall in Haean rages in $\delta^{15}N$ between -2.00 and 14.00 ‰ and is heavily enriched in ^{18}O with $\delta^{18}O$ values between 25 and 75 ‰ (Table 7).

The $\delta^{15}N$ of nitrate in stream water ranged between -1.3 $^{0}/_{00}$ and 9.9 $^{0}/_{00}$ while its $\delta^{18}O$ was between -7.8 $^{0}/_{00}$ and 11.2 $^{0}/_{00}$ (Table 7). With mean values of 5.2 ± 2.5 ‰ for $\delta^{15}N$ and 0.7 ± 3.8 ‰ for $\delta^{18}O$ nitrate in stream water was significantly ($p<0.001$) more enriched in ^{15}N and significantly ($p<0.001$) more depleted in ^{18}O than nitrate in mineral fertilizers ($\delta^{15}N$ = 1.0 ± 1 ‰; $\delta^{18}O$ = 26.9 ± 6.8 ‰) and much more depleted in ^{18}O than nitrate in rainfall. With $\delta^{15}N$ values ranging from 4.7 $^{0}/_{00}$ to 18.9 $^{0}/_{00}$ and a mean value of 11.6 ± 4.3 ‰ nitrate in groundwater was even more enriched in ^{15}N than nitrate in stream water. Simultaneously, nitrate in groundwater was more enriched in ^{18}O (range between 0.2 and 32.0 ‰; mean $\delta^{18}O$ = 13.1 ± 8.1 ‰) than nitrate in stream water.

Table 7. Nitrate $\delta^{15}N$ and $\delta^{18}O$ values in atmospheric input (rain), stream water and groundwater in the Haean agricultural sub-catchment and $\delta^{15}N$ and $\delta^{18}O$ values in mineral and organic fertilizers as used by farmers in the Haean catchment. Stream and groundwater isotopic composition where measured during pre-monsoon and monsoon season in 2013.

Haean agricultural sub-catchment						
Isotopic composition	**ð^{15}N**			**ð^{18}O**		
	Max ($^0/_{00}$)	**Ave ($^0/_{00}$)**	**Min ($^0/_{00}$)**	**Max ($^0/_{00}$)**	**Ave ($^0/_{00}$)**	**Min ($^0/_{00}$)**
Mineral fertilizers	2.7	1.0± 1.0	0.6	40.5	26.9± 6.8	20.4
Organic fertilizers	9.6	6.0± 3.4	3.4	15.1	7.3± 3.9	3.5
Rain[a]	14.0		-2.0	75		25
Stream water	9.9	5.2± 2.5	-1.3	11.4	0.7±3.8	-7.8
Groundwater	18.9	11.6± 4.3	4.7	32.0	13.1± 8.1	0.2

Rain[a] Atmospheric deposition (Lee et al., 2007)

4. Discussion

4.1 Hydrological situation in the Haean sub-catchment in the seasons 2013 and 2014

Precipitation in the monsoon season differed extremely in the two years of this investigation. In 2013 the monsoon season was characterized by rainfall amounts above the eleven-years average, (Kim et al. 2007), while in 2014 a monsoon season almost completely failed leading to rainfall amounts clearly below the eleven-years average, (Kim et al. 2007). Monsoon predictions are still challenging, however, they are of essential importance for an economy as in South Korea to ensure solid water management, water resources and water quality. Trends in precipitation rainfall, intensity and drought periods between monsoon seasons have already been assessed in several studies. All of them found a relationship between global increase in temperature and increasing extremes in monsoon precipitation. This relationship appears to be still rather complex and generates some controversy especially because of its considerable variation (Choi, 2008).

Ashfaq et al. (2009) and Cruz et al. (2012) suggested a suppression of summer precipitation, a delay in monsoon onset, an increase in the occurrence of monsoon break periods, as well as variations of total rain distribution in the east Asian summer monsoon, due to the small scale regional circulations which are more vulnerable to climate change (Rajeevan et al. 2008).

Nonetheless Wang et al., (2006) found that regardless of the large amplitude of year-to-year variations, the total summer monsoon rainfall has increased by approximately 7% per century.

Such variations in the presence of summer monsoon rainfalls can cause unpredictable hazards in terms of water quality and changes in biogeochemical and hydrological drivers of nitrate leaching as shown in this investigation. Water resource managers should consider changes in the frequency, timing, and magnitude of potential flooding or droughts, if the observed trends were to continue in the future (Chang and Kwon, 2007).

Discharge in the Haean agricultural sub-catchment was automatically related with the amount and intensity of monsoon rainfalls in both years. During the pre-monsoon season in both years of investigation no major changes along the stream were registered. Discharge within the monsoon season of 2013, however, increased in parallel with individual monsoon storm events not only due to the amount of rain, but also because of the increase in the surface runoff and river-aquifer exchange.

Our results show that spatial and temporal factors contributed to the high variability of discharge. Bartsch et al. (2013) explained this high discharge variability by river-aquifer exchange fluxes causing frequently riverbed flow reversals and suggested that the dynamics of exchange between rivers and groundwater may strongly influence the quality of water resources.

4.2 Seasonality of nitrate concentrations and fluxes in precipitation input and stream runoff in the seasons 2013 and 2014.

Nitrate concentrations in rainfall had an average of 3.1 mg L^{-1} in our study with no major variation between year of investigation and pre-monsoon and monsoon season. Our nitrate concentration data in rainfall are in agreement with other investigations in Asia. Hong et al., (2002) found that rainfall nitrate concentration in South Korea decreased in summer and had an average of 4.8 to 6.1 mg L^{-1} (between 1996 and 2000). For Asia in general rain nitrate deposition data between 0.2 and 4.7 mg L^{-1} with local and regional trends towards decreasing nitrate concentrations in the last 5 to 10 years were reported (Vet et al. 2013). Nitrate concentrations in rain in Korea are slightly higher than in Japan (Kaneyasu 1995; Wakamatsu et al. 1996; Shimohara et al. 2001), but significant lower than in China (Sun et al. 1998; Lee et al. 2000).

Our results show that total N_{NO3-} fluxes with precipitation are related with the amount of rain in both years of investigation. Nitrogen from nitrate input with rainfall during the sampling period in 2014 was 13.3% (2.1 N_{NO3}^{-} kg ha^{-1}) of the input during the same period in the year before

(16.4 N_{NO3}^- kg ha^{-1}) due to the difference in precipitation during the monsoon season. In general, the N_{NO3}^- of wet atmospheric deposition occurring in August in Asia is much related to precipitation (Yu et al. 2014).

Vet et al. (2013) showed a nitrate atmospheric deposition average value of 9.9 kg N ha^{-1} yr^{-1} in Asia. This value is in between our findings just for the sampling periods May to August in the Haean catchment in 2013 and 2014. However, when considering that rainfall during the monsoon season represents 50 – 90 % of the total annual precipitation (Kim et al. 2007) our data for N_{NO3-} input with precipitation in the Haean catchment are in agreement with the nitrate atmospheric deposition data across Asia.

In South Korea fertilizer is considered as the largest source of nitrate generation. The total national nitrogen discharged into water runoff from fertilizer is 467,778 t yr^{-1} (Kim et al. 2006). The rate of fertilizer application in the country is 5 -10 times higher than OECD average and the export rate of nitrogen from agricultural fields is much higher in South Korea than other countries (Kim 2006).

Nitrate nitrogen input with precipitation in the Haean catchment turned out to be low in comparison to the annual nitrogen fertilizer applications in the agricultural parts of the catchment. For the agricultural sub-catchment the average mineral nitrogen fertilizer application is estimated to be 313 kg N ha^{-1} yr^{-1} (Kim et al. 2008). In addition to this mineral fertilizer application organic fertilizer applications with an additional nitrogen input between 110 (Maharjan 2015) and 134 kg N ha^{-1} yr^{-1} (Yanggu Office 2014) are common practice. Based on this mineral fertilizer application and not considering the additional organic nitrogen fertilizer the nitrate nitrogen input by precipitation contributed not more than 5.2% in 2013 and 0.7% in 2014 to the entire mineral nitrogen input in the investigated Haean sub-catchment. Thus, based already on this comparison, nitrate input by precipitation is unlikely to be a major contributor to the nitrate output by stream runoff in the Haean sub-catchment.

Average nitrate concentrations in stream runoff within the investigated Haean sub-catchment increased consistently from the uppermost forest part through the agricultural dryland to the rice paddies part and reached at the lowermost sampling point values of slightly below or above 20 mg L^{-1}. This concentration increase suggests a preferential contribution of the agricultural parts in the catchment to the nitrate runoff. Single measurements of nitrate concentrations in stream runoff varied in wide ranges from 0.4 to 64.1 mg L^{-1}. The legal limit for nitrate in drinking water in South Korea of 10 mg N_{NO3-} L^{-1} = 44 mg NO_3^- L^{-1} (Ward et al. 2005; World Health

Organization 2011; Cheong et al. 2012) was exceeded in the stream runoff only in a few cases. Nonetheless, mean concentrations of about 20 mg L^{-1} in the stream runoff indicate already a high potential for huge amounts of total nitrate output from the Haean sub-catchment.

Calculation of total N_{NO3}^- amounts in the stream discharge confirm this expectation. With increasing frequency of rain events during the monsoon period in 2013 the total N_{NO3-} amount in the stream discharge increased dramatically. It contributed 90% to the total discharge from the whole sampling campaign. Due to missing pronounced monsoon rainfalls in 2014, the proportional contribution of N_{NO3}^- in the stream discharge was not different from the N_{NO3}^- stream discharge during its corresponding dry pre-monsoon season. Thus, monsoon rains and their intensity are the main drivers for heavy N_{NO3}^- losses by runoff from the Haean catchment.

Kettering et al. (2012) also found that nitrate export was higher during monsoon season and lower export of nitrate was observed during the beginning and end of the growing period in Haean.

The forest part of the investigated sub-catchment contributed only to a minor part to the total N_{NO3}^- discharge. This finding is in agreement with observations by Shim and Kim (2005).

Total N_{NO3}^- river discharge from dryland fields was higher than from rice paddies in 2013. On the other hand, in 2014 N_{NO3}^- river discharge had no significant differences between both types of fields suggesting once more that nitrogen fluxes are closely related with heavy monsoon rain events.

4.3 Groundwater nitrate

Natural groundwater sources not affected by anthropogenic activities usually have nitrate concentrations that not exceed 3 mg L^{-1} (Burkart and Kolpin 1993). In the Haean agricultural sub-catchment nitrate concentration in groundwater ranged between 0.3 to 67.0 mg L^{-1}. As shown by a lot of previous studies (e.g. Böhlke, 2002; Choi et al., 2011; Kraft and Stites, 2003; Martin et al., 2004; McLay et al., 2001; Min et al., 2003; Oren et al., 2004; Thorburn et al., 2003), the higher end of this range is caused by agricultural activities and mostly by the use of inorganic fertilizers in crop production. Our results showed no differences in groundwater nitrate concentrations between pre-monsoon and monsoon season suggesting no dilution in concentrations during heavy precipitation. But there was a significate difference between dry land and rice paddies groundwater nitrate concentrations. In the dry land patch nitrate concentrations ranged from 0.3 to 39.4 mg L^{-1} while rice paddies groundwater was characterized

by much elevated nitrate concentrations that ranged from 18.0 to 67 mg L^{-1}. A considerable number of groundwater samples, exclusively from the rice paddy wells, exceeded the legal limit for nitrate in drinking water in South Korea of 10 mg N_{NO3-} L^{-1} = 44 mg NO_3^- L^{-1} (Ward et al. 2005; World Health Organization 2011; Cheong et al. 2012). This suggest that mineral fertilizer application in the study area generates an impact on the biogeochemical processes behind the nitrate groundwater contamination (McLay et al. 2001; Kaown et al. 2009).

The difference in nitrate concentration is also an indicator for the influence of distinct land uses on the water quality in aquifers. The middle upstream part of this altitudinal gradient in the study area was influenced by many dry land fields with top sandy layers and deeper clay layers with poor leaching capacities and therefore it is feasible that nitrate percolation from these agricultural fields to groundwater is somehow reduced or slow. It is also possible that denitrification consumes a considerable amount of nitrate in dry land fields as well as in rice paddies but in a different rate (see below).

4.4 Identifying the origin and fate of nitrate in the Haean sub-catchment based on stable isotope abundances

In principle, the nitrate detected in the stream runoff and in the groundwater in the investigated Haean sub-catchment can have four different origins: (1) Atmospheric nitrate deposition, (2) direct nitrate leaching from the mineral fertilizers applied to the dryland and rice paddy fields, (3) microbial mineralization and subsequent nitrification of soil organic compounds and/or nitrification of ammonium in mineral fertilizers and (4) nitrate of either of the above origins that underwent partially microbial denitrification under anaerobic/sub-aerobic conditions. In the following we use our stable isotope abundance data to sort out the relevance of any of these four potential nitrate sources.

(1) Atmospheric nitrate deposition: Due to involvement of ozone in atmospheric nitrate formation nitrate from deposition in general is characterized by unique enrichments in ^{18}O (Durka et al. 1994; Kendall et al. 1995, 1996; Kendall and McDonnell 1998). In agreement with this general observation, Lee et al. (2008) reported $\delta^{18}O$ values between 25 and 75 ‰ for atmospheric nitrate deposition in the northern part of South Koreas. These $\delta^{18}O_{NO3-}$ values are considerably higher than those found in our investigation for nitrate in the stream runoff in the Haean agricultural sub-catchment (Fig. 6). Thus, despite of overlaps in the $\delta^{15}N_{NO3}$- in stream runoff and atmospheric nitrate deposition we conclude that nitrate directly originating from atmospheric deposition contributed to a

rather minor proportion, if any, to the nitrate found in stream runoff. This conclusion is in agreement with the finding of a rather minor contribution of nitrate nitrogen input with precipitation in the Haean catchment in comparison to the annual nitrogen fertilizer applications in the agricultural parts of the catchment (see above).

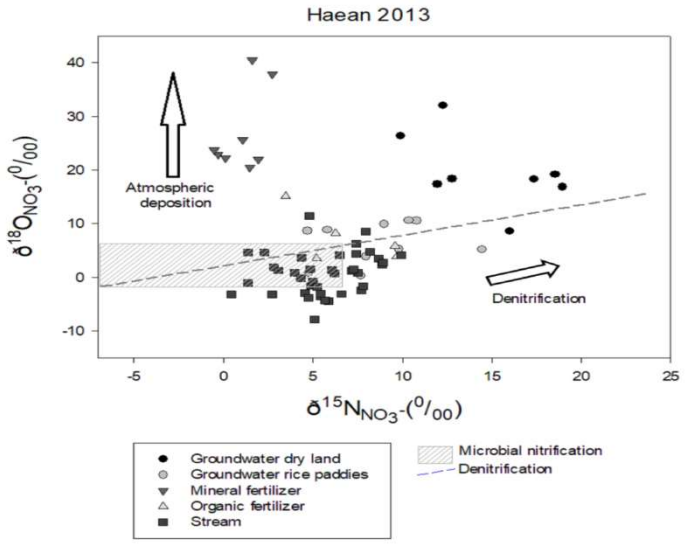

Fig. 6. Nitrate $\delta^{15}N$ and $\delta^{18}O$ isotopic composition from different sources: mineral fertilizers, organic fertilizers, atmospheric nitrate deposition (rain) that may influence nitrate discharge runoff in Haean agricultural sub-catchment. Stream and groundwater isotopic composition where measured during pre-monsoon and monsoon season in 2013. Calculated theoretical microbial nitrification and denitrification for the site is represented by the striped box and broken line respectively.

(2) Direct nitrate leaching from mineral fertilizers: In Haean, specifically in the cropland area, farmers often add sandy soil and high amounts of mineral and organic fertilizers on the top of the fields due to the high soil erosion rates during monsoon season (Berger 2012; Kettering et al. 2013). This activity occurs almost every year in the beginning of the growing season between May and June. Therefore, high rates of mineral fertilizers might be expected in the discharge runoff during the monsoon season, which occurs within a few weeks after the mentioned soil treatments (Kettering et al. 2012; Bartsch 2013).

Mineral fertilizers applied in the study area have $\delta^{15}N_{NO3-}$ (mean: 1.0 ± 1.0 ‰) and $\delta^{18}O_{NO3-}$ (mean: 26.9 ± 6.8 ‰) values in the typical range known in general for synthetic fertilizers of (Kendall 1998). Nitrate in mineral fertilizers originates from atmospheric nitrogen ($\delta^{15}N$ = 0 ‰) and oxygen ($\delta^{18}O$ = ~23.5 ‰) (Amberger and Schmidt 1987) $\delta^{18}O$ and $\delta^{15}N$ values as found for nitrate in the stream runoff in the investigated Haean sub-catchment were consistently less enriched in ^{18}O and in most cases more enriched in ^{15}N

than in the mineral fertilizers (Fig. 6). Thus, nitrate leached directly from mineral fertilizers into the stream runoff is obviously also only a minor contributor to the nitrate discharge.

(3) Microbial mineralization and subsequent nitrification of soil organic compounds and/or nitrification of ammonium in mineral fertilizers: In aim to compare isotopic composition of nitrate as found in the stream runoff with nitrate originating from soil microbial nitrification, we calculated ranges that should theoretically be expected for nitrate from soil microbial nitrification (shaded bar in Fig. 6). The theoretically expected isotopic composition of nitrate from nitrification is based on $\delta^{15}N_{NO3-}$ values reported from the literature (Hübner 1986; Amberger and Schmidt 1987; Kendall and McDonnell 1998) and ranging between ~-6 and +6 $^{0}/_{00}$ and on $\delta^{18}O$ values that are based on the physiology of microbial nitrification and local conditions (Durka et al., 1994; Ohte et al., 2004; Wassenaar, 1995; Kendall, 1998). One of the three oxygen atoms in the nitrate molecule originates from atmospheric O_2 ($\delta^{18}O$ ~+23.5 ‰). The other two oxygen atoms originate from soil water. The isotopic composition of soil water is mostly driven by the isotopic composition of local precipitation, which ranges in $\delta^{18}O$ in the Haean catchment during the summer season between -13.5 and -5.5 ‰. Based on these facts we can expect for nitrate from microbial nitrification $\delta^{18}O$ values between ~ -1.3 and + 4.9 $^{0}/_{00}$. The majority of nitrate isotope abundances found in the stream runoff fall into the range or is close to the range expected for nitrate from soil microbial nitrification (Fig. 6). Thus, we conclude that a major part of the nitrate in the stream runoff does not originate from direct fertilizer leaching, but underwent microbial nitrification before leaching. A wide range of precursors can contribute to the nitrate that underwent microbial nitrification before appearance in the stream runoff: mineralized and nitrified soil organic matter that ultimately originates from decomposed plant material, mineralized and nitrified organic fertilizers or nitrified ammonium from mineral fertilizers. Nonetheless, some of the stream runoff samples and all groundwater samples do not fall into the range of $\delta^{15}N$ and $\delta^{18}O$ values as to be expected for nitrate from microbial nitrification (Fig. 6). These samples are more enriched in ^{15}N and simultaneously in ^{18}O and thus, can neither be explained by nitrate from atmospheric deposition or mineral fertilizers nor by soil microbial nitrification.

4) Nitrate of the origins (1) to (3) that underwent partially microbial denitrification under anaerobic/sub-aerobic conditions: In microbial denitrification nitrate is reduced under

anaerobic/sub-aerobic conditions and consumption of easily accessible organic carbon compounds via NO to N_2O or ultimately to N_2. Denitrification is associated by a high isotope fractionation, i.e. denitrification products are depleted in ^{15}N and ^{18}O and the remaining nitrate that not yet underwent denitrification becomes automatically enriched in ^{15}N and ^{18}O following the principles of Rayleigh distillation (Mariotti et al. 1988; Kendall 1998; Min et al. 2003). This systematic shift in the isotopic composition of the remaining nitrate happens in a relationship **2** $(\delta^{15}N)$ **: 1** $(\delta^{18}O)$ (Amberger and Schmidt 1987; Böttcher et al. 1990; Kendall 1998). The direction of this isotopic shift is indicated by the hatched line in Fig. 6. Our isotope abundance data show that specifically nitrate in groundwater was under the influence of denitrification. The $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in groundwater ranged between ±4.7 and ±18.9 $^{0}/_{00}$ or 0.2 and 32.0 $^{0}/_{00}$ respectively, with nitrate in the groundwater from the dry land wells covering the more positive and nitrate in the groundwater from the rice paddy wells covering the less positive end (Fig. 6). Thus, nitrate in the groundwater of the dry land area is apparently more under the influence of denitrification than nitrate in the groundwater of the rice paddy area. Kim et al. (2015) provided already evidence for a strong influence of denitrification on the groundwater nitrate in the Haean agricultural catchment.

Previous investigations in the Haean catchment have also already shown that specifically in the monsoon season groundwater contributes to the aquifer, hence to the river discharge. Bartsch et al. (2014) found that monsoonal precipitation events affect the dynamic of the river- aquifer with exchange fluxes between groundwater and the riverbed water. During pre-monsoon season and also after monsoon season the rivers in the study area were in a stage of "losing stream", where water enriched in DOC is pushed into the nitrate rich groundwater. These dynamics probably create perfect conditions for microbial denitrification within the groundwater. During monsoon season rivers that were in a "losing stream" pass to a "gaining stream" stage where nitrate-rich groundwater likely influenced by denitrification, contributed to river water.

Our results of nitrate isotope abundance in the river discharge show for some samples ^{15}N and ^{18}O values that are above the range to be expected for nitrate originating exclusively from microbial nitrification (Fig. 6). This ^{15}N and ^{18}O can be explained by the river-aquifer exchange where ^{15}N and ^{18}O enriched nitrate from groundwater is mixed with isotopically less enriched nitrate from the stream water. Interestingly, ^{18}O enriched nitrate tended to appear more frequent in the steam runoff with onset of the monsoon season in 2013 (Fig. 7). This trend towards higher

$ð^{18}O_{NO3-}$ in the river water during the season was confirm statistically (P<0.800) exclusively for the last values corresponding to the onset of the monsoon.

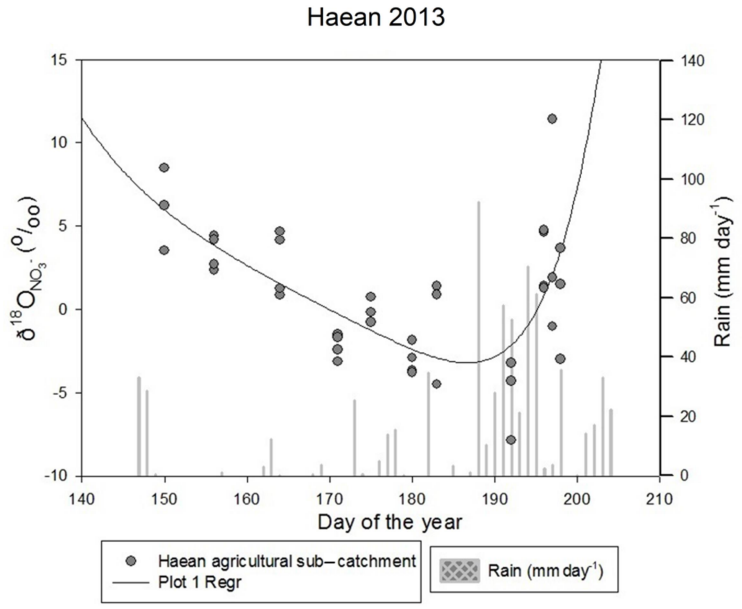

Fig. 7. Nitrate ð18O values from stream samples during pre-monsoon and monsoon season 2013 compared with the total rainfall per day and precipitation events in the investigated Haean agricultural sub -catchment. All the sampling points are included in this graph.

Based on the indications of a nitrate flow from groundwater to river water exclusively during the extremely wet monsoon season in 2013 we assumed a missing groundwater-to-river-water nitrate flow for the dry monsoon season in 2014. In order to test this assumption and due to the fact of lacking nitrate $\delta^{18}O$ data for 2014 we used a different approach proposed by Mariotti (1981, 1988) and Kendall (1998) to identify denitrification-affected nitrate in the river water samples collected in 2013 and 2014. This approach is based on a test for significance of correlations between nitrate $\delta^{15}N$ and the inverse natural logarithm of nitrate concentrations in the river runoff. A significant correlation between nitrate $\delta^{15}N$ and the inverse of nitrate concentrations indicates that dilution is not responsible for the observation of low nitrate concentrations, but rather suggests that river runoff nitrate was at least partially affected by denitrification and accompanying ^{15}N enrichment.

As shown in Fig. 8 we found a weak (r = 0.326), but nonetheless significant (P<0.050) correlation between nitrate $\delta^{15}N$ and the inverse natural logarithm of nitrate concentrations in the river water for 2013, but not for 2014 (r = 0.196, P>0.050). Thus, these data corroborate our

assumption of a groundwater-to-river-water nitrate exchange only under conditions of heavy monsoon rainfall.

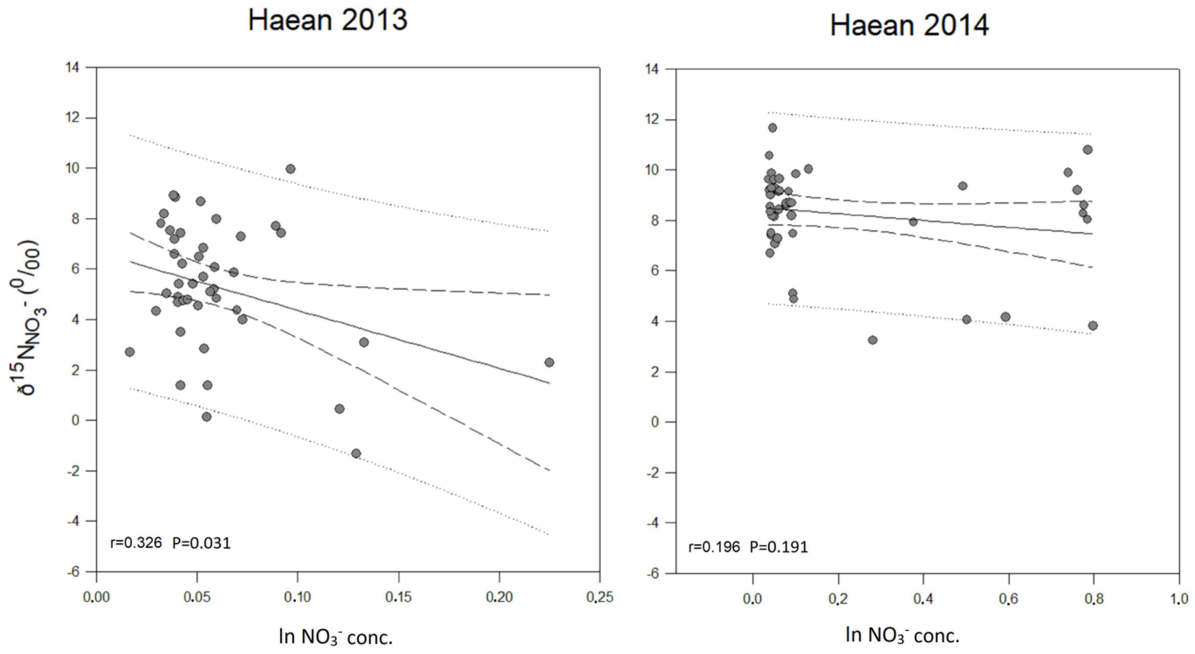

Fig. 8. Correlation between $\delta^{15}N_{NO3^-}$ and inverse nitrate concentration in discharge runoff in the investigated Haean agricultural sub- catchment during the growing season 2013 and 2014.

5. Conclusions

Heavy rainfalls in the monsoon season of 2013 turned out as drivers of huge nitrate leaching in the river runoff of the agricultural Haean sub-catchment investigated here. In contrary, an almost completely missing monsoon season in 2014 reduced the nitrate leaching in the river runoff by several orders of magnitude. Thus, increased monsoon precipitation as predicted by global climate change scenarios for Southeast Asia in the future may even increase nitrate leaching from the Haean agricultural sub-catchment and seriously affect the quality of the Soyang lake drinking water reservoir. In order to avoid an increase of nitrate leaching from the Haean agricultural sub-catchment or better achieve reduced nitrate leaching a considerable reduction of nitrogen fertilizer application by local farmers is required. A specifically critical role in this framework is played by the dry land farming in the lower slopes of the Haean catchment. Regional decision makers are fully aware of this problem and initiated a change of agricultural practices. A switch from annual crop growing towards less fertilizer demanding and soil erosion

preventing perennial crops, like ginseng, vinyards and orchards, is currently on the way (MAFRA 2013, 2014; Yanggu Office 2014).

Based on our isotope abundance analyses neither atmospheric nitrate deposition nor direct nitrate fertilizer leaching contributed significantly to the nitrate found in the river runoff. The majority of the leached nitrate rather originated from microbial nitrification. This finding indicates by no means that the applied nitrogen fertilizers were not the precursors of the leached nitrate. Probably all nitrogen fertilizers (mineral fertilizers and organic fertilizers) plus soil organic matter and residues of the crop plants served as substrates for microbial nitrification leading to the nitrate ultimately leached to the river runoff. Nitrate from the groundwater specifically from the dry land area and previously affected by microbial denitrification contributed considerably in periods of heavy monsoon rainfall to the nitrate in the river runoff.

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Chapter 3

The fate of monsoonal atmospheric nitrate deposition in two forest catchments in Soyang lake watershed, South Korea – A mass balance and stable isotope approach

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Abstract

More than 60% of the entire area of South Korea is covered by deciduous, coniferous or mixed forests. Atmospheric nitrate deposition plays an important role as nitrogen source in these forests.

We compared with a mass balance approach the atmospheric nitrate input and output by stream runoff in two forest sub-catchments, a deciduous and a mixed catchment, within the Soyang lake watershed, the main drinking water reservoir for the 20 million metropolis Seoul. A dual stable isotope approach ($\delta^{15}N$ and $\delta^{18}O$) was used to identify the origin (atmospheric nitrate deposition or soil microbial nitrification) of nitrate in stream discharge of the two sub-catchments.

Extremely different monsoon seasons in 2013 and 2014 drove the nitrate discharge from both sub-catchments. Total nitrate-N export was closely related with rainfall events and intensities. Nitrate-N discharge at the deciduous forest was lower than atmospheric nitrate-N deposition, thus sink conditions prevailed. Nitrate-N discharge at the mixed forest was consistently higher than at the deciduous forest. During the heavy monsoon season of 2013 the mixed forest turned from a sink for atmospheric nitrate towards a source, i.e. nitrate amounts in the discharge were higher than atmospheric inputs. Nitrate isotopic compositions of stream water from both forests revealed microbial nitrification as main nitrate source. However, under conditions of heavy monsoon rainfall direct runoff of atmospheric deposition nitrate was identified in the mixed forest.

Lower nitrate assimilation capacities of conifers compared to deciduous trees are probably the drivers for the lower nitrate retention capacity of the mixed forest sub-catchment.

Keywords

Nitrate; Monsoon, Stable isotope; Atmospheric deposition; Retention capacity; Microbial nitrification

1. Introduction

Natural forest ecosystems are adapted to limited nitrogen availability and the dynamics between all the living elements that intervene in the nitrogen cycle function optimally under this condition (Vitousek et al. 1997). In striking contrast to this property developed over long terms in evolution is the dramatic alteration of the global nitrogen cycle due to human activities during the last decades (Vitousek et al. 1997; Aber et al. 2003; Galloway et al. 2003) that has increased by nine times the nitrogen mobilization from the Earth's crust and atmosphere into the environment since pre-industrial times (Galloway et al. 2014). These activities have accelerated the nitrogen cycle, transformed ammonium, nitrate and organic nitrogen sources, altered the biogeochemical processes of natural ecosystems, changed the rates and pathways of nitrate leaching (Berendse et al. 1993) and last but not least, they have influenced the natural nitrogen isotopic composition of forest ecosystems (Denk et al. 2017).

Nitrogen compounds of anthropogenic origin enter natural forest ecosystems predominantly by atmospheric deposition to the tree canopy and to the forest floor (Gebauer et al. 1994; Nadelhoffer and Fry 1994). The responses of by nature nitrogen-limited forest ecosystems to increases in nitrogen availability depend, among other factors, on the forest species composition (Aber et al. 1998, 2003; Lovett et al. 2000, 2002). Although most northern forests are efficient at retaining nitrogen from atmospheric input (Aber et al. 1989; Harrison et al. 2000), natural forested areas can seriously become affected by chronic atmospheric nitrogen deposition (Schulze 1989; Aber et al. 1989, 2003; Vitousek et al. 1997; Lovett et al. 2000). Over time continuous nitrogen additions affect the nitrogen uptake and retention capacities by plants, soils and microbes (Vitousek et al. 1979; Friedland et al. 1984; Nihlgard 1985; Reuss and Johnson 1986; Rascher et al. 1987; Aber et al. 1989, 1998, 2003). It also increases nitrification rates in forest soils, raises nitrate losses into streams (Smith et al. 1968; Vitousek et al. 1979; Durka et al. 1994; Aber et al. 1998, 2003; Driscoll et al. 2003), and leads in the long term to nitrogen saturation of entire ecosystems (Aber et al. 1989). In this sense the South Korean peninsula faces a real challenge with chronic nitrogen input from atmospheric deposition into their forest resources (Lee et al. 2000, 2012; Hong et al. 2002), together with the risk of high nitrate output through the soils into streams due to heavy rainfall in the monsoon seasons (Bartsch et al. 2013, 2014).

South Korea has about 70% of mountainous area (MAFRA 2013) and the total forest land use is about 64.1% (Korean Forest Service 2013). The forests are categorized as natural (85%) and

artificial (15%) (Korean Forest Research Institute 2013) with the latter ones located in catchments around the highly populated metropolis of Seoul. Deciduous forests represent 27% of the forested area, while coniferous and mixed forests are 41% and 29%, respectively (Korean Forest Service 2013; Kim et al. 2017). Korean forests are relatively young. During Korean War the forests were excessively devastated. A large-scale reforestation program post–war was established in 1973 to rehabilitate forests. This program reforested 1.7 million hectares of degraded land with a total of 12 billion trees (Lee et al. 1997; Korea Forest Service 2014; Lee 2015).

South Korea receives a great amount of rainfall during the East Asian summer monsoon season. This period of intense precipitation produces high impact on the drinking water reservoirs, due to pollutants derived from non- point sources. In forested areas, monsoon season is an important driver for many biogeochemical and hydrological processes (Berger et al. 2013). Rainfall intensity and timing of summer monsoon seasons have become increasingly variable in the last years due to global climate change (Ho et al. 2003; Chang and Kwon 2007; Ashfaq and Trapp 2009; Kim et al. 2012). This can affect greatly the nitrogen cycle dynamics and also produce a change in the forest assimilation capacities, soil retention and nitrate sources.

Thus, there is an increasing demand for studies investigating effects of extremely different weather conditions on nitrate inputs and outputs not only in agriculture dominated watersheds but also in semi-natural forest watersheds. Such investigations become even more urgent, when drinking water reservoirs are affected by nitrate inputs, like in the Soyang lake watershed, which is the main drinking water reservoir for the 20 million metropolis Seoul.

The objectives in this study are: (1) To evaluate the assimilation and retention capacities of two different forest sub-catchments within the Soyang lake watershed, a pure deciduous tree and a mixed, but still conifer-dominated catchment, using a nitrate mass balance assessment. We evaluate the influence of two extremely different monsoon seasons on atmospheric nitrate input and nitrate leaching from soils. Considering summer rainfall inputs from a monsoon season (2103) with precipitations above the eleven years average (Kim et al. 2012), and an almost failed monsoon season (2014) with rainfalls clearly below the average, we develop scenarios for nitrate exports from forest catchments in summer monsoon climate regions under conditions as predicted by global climate change scenarios. (2) To use a dual stable isotope technique to identify and compare the fate of nitrate in the two different forest types of this investigation. Simultaneous measurement of $\delta^{15}N$ and $\delta^{18}O$ from nitrate on natural abundance level (Amberger

and Schmidt 1987; Revesz et al. 1997; Silva et al. 2000) allows separating the origin of nitrate (atmospheric deposition versus soil microbial nitrification) in the river runoff (Durka et al. 1994; Wassenaar 1995; Aravena and Robertson 1998; Mayer et al. 2001; Mengis et al. 2001). We hypothesize that conifer-dominated forests are more prone to nitrate leaching than deciduous forest, because of a lower nitrate assimilating capacity of conifers (Gebauer and Schulze 1997). (3) To evaluate the $\delta^{15}N$ of nitrate along soil depth gradients and compare these data with depth gradients of total nitrogen $\delta^{15}N$ values. Forest soils are characterized by a typical increase in $\delta^{15}N$ from litter layer down to mineral soil and simultaneous decrease in total N concentration (Nadelhoffer and Fry 1988; Gebauer and Schulze 1991; Garten and Van Miegroet 1994; Gebauer et al. 1994; Emmett et al. 1998). This pattern reflects an isotopic discrimination of ^{15}N during mineralization of soil organic nitrogen. Based on these facts Nadelhoffer and Fry (1994) developed a hypothetical model predicting that nitrate from microbial nitrification follows the same depth gradient, i.e. nitrate produced in the litter layer is more depleted in ^{15}N than nitrate produced in the mineral soil. Here we use our dataset as a side product to test this hypothetical model under field conditions.

2. Materials and Methods

2.1 Research site

The study was conducted in two forest sub-catchments within the Soyang lake watershed. This basin is located in the Gangwon-do province in the northeast part of South Korea. The total area of the watershed is 2,675 km^2. Most of the Soyang watershed area is dominated by forested mountainous land (over 85%). The mean annual air temperature is 10.5°C with minimum monthly temperature of -10°C in January and maximum monthly temperature of 27°C in August (1999 - 2013). Annual average precipitation is 1300 mm and between 50 – 60 % of the annual rainfall happens during the summer monsoon period (July – Sep) (WAMIS).

The first sub-catchment is a pure deciduous forest (D) within the Haean agricultural basin (Lat. 38.251532, N 128.11991 Long. W, 586- 1005 m asl). The sub-catchment is dominated by tree species as *Juglans mandshurica*, *Acer pictum*, *Quercus dentata*, *Quercus mongolica*, and *Fraxinus rhynchophylla.* The entire deciduous sub-catchment area is 39.78 ha. Acid Cambisols are the typical soils in the Korean forested mountain slopes (Jeong et al. 2012; FAO IUSS Working Group WRB 2014) and particularly in this site the organic cover (0-20 cm) has distinct Oi and less distinct Oe/Oa layers, while the mineral soil (30-60 cm) is loam texture.(Lee et al. 2016).

The second studied sub-catchment is a mixed (coniferous/deciduous) forest (M) located in Seohwa outside of the Haean agricultural basin, 6 km distance from the pure deciduous site (Lat. 38.206828 N, Long. 128.185719 W, 368-682 m asl). The total area of the mixed sub-catchment is 15.6 ha with 6.1 ha of coniferous forest (39%) and 9.5 ha of deciduous forest (61 %). The mixed forest sub-catchment is dominated by coniferous trees including *Larix kaempferi* and *Pinus densiflora*, in the lower part of the basin. The upper part of the mixed sub-catchment is dominated by deciduous trees including *Juglans mandshurica*, *Acer pictum*, *Quercus dentata, Tilia amurensis* and *Ulmus davidiana*. In analogy to the pure deciduous sub-catchment the the mineral soil (30-60 cm) has loam texture with an organic layer (0-20 cm) conformed by a distinct Oi and a less distinct Oe/Oa layer. (Lee et al. 2016).

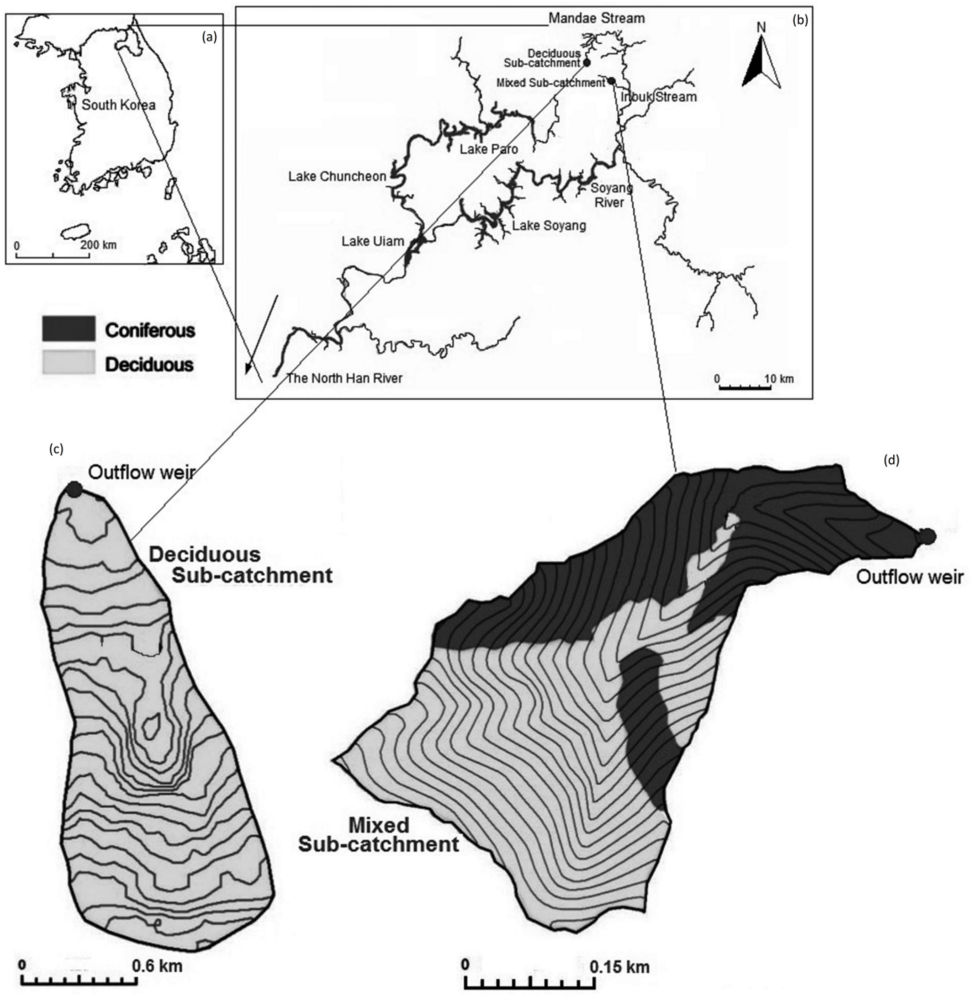

Fig 1. Location of the investigated forest sites (a) in the northeastern part of South Korea (b) within Soyang lake watershed. (c) deciduous sub-catchment (d) mixed sub-catchment.

2.2 Field instrumentation and data collection

Equal instrumentation was installed in both forest sites. Stream, rain, throughfall (sampling in 2013 and 2014) and soil water samples (sampling only in 2014) were collected for nitrate concentration and stable isotope abundance analysis. The sampling design was made to determinate the influence of the precipitation regime and type of forest in the sources and total nitrate discharge into Mandae River, one of the most important streams in the Soyang lake watershed.

During the field campaign 2013, all the samples were collected every second day and after every rain event in the dry pre-monsoon season. During heavy monsoon season samples were collected after rain events up to every six hours in precipitation events that lasted at least 12 hours. During the field campaign in 2014 the samples were collected after every rain event due to the low amount and intensity of rainfall. Especially during growing season 2013 two periods were accounted for the sampling collection, a dry pre-monsoon season (May – June) and a monsoons season (July- August). During growing season 2014 we still divided the sampling periods in dry pre-monsoon (June) and a monsoon season (July – August), although in this year these two period could not be differentiated due to the lack of monsoon rainfalls.

Stream samples were collected using an automatic collector (6712 Portable Sampler, Teledyne Isco Inc., Lincoln, NE, USA). Rain samples were collected with bulk precipitation samplers installed in an open area near the plots. Throughfall samples were collected from samplers under the forest canopy. In both cases the samplers were at 1 meter distance from the ground. Soil water was sampled in different depths. Water from the soil organic layer (10 – 20 cm) was sampled using cero tension plates installed beneath the organic layer. Water from the mineral soil layer (30 - 60 cm) was sampled using ceramic suction cups installed in 10 cm intervals. Extra pH measurements were taken from the diluted soil water at the same depths with a gel electrode (SenTix 21 Gelelectrode DIN-Cable, WTW GmbH & Co, Weilheim, Germany).

All samples were stored in 1 litter plastic bottles for isotope analysis and in 2 ml tubes for nitrate concentrations. After collected, the samples were immediately frozen and stored for their subsequent transport to Germany for the analysis. In aim to keep the samples frozen during the transportation, dry ice was added to the cooling boxes.

Analysis of nitrate concentration and isotope abundance were completed at the Hydrology Department and Isotope Biogeochemistry Laboratory of Bayreuth University, respectively.

2.3 Weir locations and discharge calculations

River discharge was measured with two V-notch weirs located in the outflow of each sub-catchment (Fig. 1) (Ackers et al. 1978; Chanson and Wang 2012, 2013). Water level and barometric data used in discharge calculations were measured at the weir with absolute pressure transducers, which recorded total head at 5 min intervals (Levelogger® Edge Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada) and barologgers (Barologger Edge Model 3001, Solinst Canada Ltd, Georgetown, Ontario, Canada) for barometric compensation. V-notch weir discharge values were calculated using the Kindsvater and Shen formula (Kulin and Compton 1975; El-Ansary et al. 2010).

2.4 Weather stations and rainfall measurements

Precipitation was recorded at 5 min intervals using an automatic weather station (WS-GP1, Delta-T Devices, Cambridge, UK) located in an open place near the sites. Data from the bulk precipitation samplers were also measured.

2.5 Laboratory analysis

2.5.1 Nitrate concentration analysis

Rain, throughfall, stream and soil water samples were analyzed for nitrate concentration using an anion exchange high performance liquid chromatograph (HPLC) and subsequent UV detection (HPLC LC4000 Jasco Europe S.r.l., Cremella, Italy) using PeakSimple Chromatography software (PeakSimple 3.93) and an anion exchange IC column (VYDAC 302IC 10µm Anion Exchange 250 x 4.6mm, Grace Corporate Headquarters, Columbia, USA). The samples were unfrozen inside of a refrigerator at 4^{o}C 12 hours before the analysis.

2.5.2 Sample preparation and isotope analysis

Nitrate extraction from each water sample as described by Huber et al. (2011) was required before their subsequent isotope abundance analysis. The procedure consisted of the following steps:

1. *Removal of the bound water molecules using a freeze–drying technique*: First we unfroze the 1 L stream and soil water samples in a refrigerator at 4° C for 24 h. Then we transferred the water samples into glass vessels, froze the samples at -40°C in a salt/ethanol bath and completed freeze-drying of the samples in the following freeze-

drying machines: Freeze Dryer condenser EF4 Modulyo with two levels of 12 port acrylic lid, Edwards High vacuum B.O.C. Ltd, Crawley, England and SuperModulyo freeze dryer 20 L with Column manifolds 24 port, Edwards High vacuum B.O.C. Ltd, Crawley, England.

2. *Nitrate isolation by the precipitation of $Ba(NO_3)_2$ (Huber et al. 2011):* We added a NaI + acetone + hexane solution to the samples. Insoluble compounds sank overnight in a refrigerator to be subsequently centrifuged (Beckmann J6 High Capacity Centrifuge, Beckmann Coulter, Krefeld, Germany). Then we transferred the supernatant into new centrifugation tubes and added BaI_2 diluted in acetone to precipitate $Ba(NO_3)_2$. After settling of the precipitate in a refrigerator and its corresponding centrifugation, we decanted each sample and dried the $Ba(NO_3)_2$ at 60°C overnight. We dissolved the $Ba(NO_3)_2$ in defined water volumes and transferred the aliquots into tin (for N isotope abundance analysis) or silver capsules (for O isotope abundance analysis) and again complete dried the samples before closure of the capsules.

Relative nitrogen isotope abundances of the nitrate samples ($\delta^{15}N_{NO3-}$) were measured with an elemental analyzer (Carlo Erba 1108, Milano, Italy) for Dumas combustion followed by gas chromatography and feeding of N_2 into a continuous flow isotope ratio mass spectrometer (delta S Finnigan MAT, Bremen, Germany) via a ConFlo III interface (Thermo Fisher Scientific, Bremen, Germany) as described by Bidartondo et al. (2004). Nitrogen standard gas was calibrated with respect to the international standard (N_2 in air) by using the reference substances N1 and N2 provided by the IAEA (International Atomic Energy Agency, Vienna, Austria). Nitrogen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard acetanilide with known nitrogen content of 10.36% (Gebauer and Schulze 1991). For recovery control of our extraction procedure nitrogen amounts in a randomly selected sample subset were compared to the independently by HPLC measured nitrate concentrations. Nitrogen recovery was always close to 100%.

Relative oxygen isotope abundances of the nitrate samples ($\delta^{18}O_{NO3-}$) were measured by thermal conversion through pyrolysis (HTO, HEKAtech, Wegberg, Germany) followed by gas chromatography and feeding of CO into a continuous flow isotope ratio mass spectrometer (delta V advantage Thermo Fisher Scientific) via a ConFlo IV interface (Thermo Fisher Scientific) as described by Gebauer et al. (2016). The CO standard gas was calibrated with respect to the international standard (SMOW) by using the reference substances IAEA601 and IAEA602

provided by the IAEA. Oxygen amounts in the samples were calculated from peak areas using a six-point calibration curve per sample run based on measurements of the laboratory standard benzoic acid with known oxygen content of 26.20%. For recovery control of our extraction procedure oxygen amounts in a randomly selected sample subset were compared to the independently by HPLC measured nitrate concentrations. Oxygen recovery was close to 100% for the nitrate extracted from water collected in 2013. However, for the nitrate extracted separately from water collected in 2014 oxygen recovery exceeded the 100% threshold significantly. Thus, for the 2014 samples the isolated nitrate was obviously still contaminated with other oxygen-containing compounds for unknown reason. Thus, all $\delta^{18}O_{NO3-}$ data of the 2014 sample collection were not considered for any further data presentation.

2.5.3 Nitrate fluxes, isotope calculations and statistical analysis

Nitrate flux calculations were carried out using the calculated N_{NO3}^- from nitrate concentrations multiplied by the total stream area discharge and rain input per day. Nitrate fluxes were measured in both years 2013 and 2014. We calculated fluxes in rain input using bulk precipitation and throughfall data, because during heavy monsoon rainfall no major differences in nitrate concentrations of rain between under and out-canopy could be registered.

Statistical analysis and graphs were carried out using the statistical software package SigmaPlot (Windows version 11, Systat Software GmbH, Erkrath, Germany). A simple linear fitting regression with significance level of $P \leq 0.05$ was run in the program for all isotope data. Correlation analyses were run between nitrate concentrations, fluxes and rain data.

Stable isotope abundance results from nitrate in stream water in 2013 were plotted together with the natural abundance from the major nitrate sources that may influence aquifers (Kendall 1998) as microbial nitrification and atmospheric deposition.

A theoretical microbial nitrification was calculated to compare this source with the stream and soil water isotope abundance data in the research area. Nitrification of soil organic nitrogen has two thirds of oxygen from soil water (-3.5 $^0/_{00}$ and -5.5 $^0/_{00}$, OIPC; Bowen et al. 2005; Bowen 2008) and one third of oxygen from atmospheric oxygen (~ +23.5 $^0/_{00}$) (Wassenaar 1995). If we assume that the oxygen from the mentioned sources did not have any fractionation processes before their incorporation to form NO_3^-, we can calculate the theoretical microbial nitrification for the forested sub-catchments by using the following equation:

$\delta^{18}O_{NO3-} = {}^{2}/_{3}\,(\delta^{18}O_{H2O}) + {}^{1}/_{3}\,(\delta^{18}O_{O2})$.

Stable isotopes from atmospheric rain deposition were obtained from Lee et al. (2008).

3. Results

3.1 Hydrological and Weather Features

Extremely different weather conditions characterized the two years of investigation, 2013 and 2014. During the growing season in 2013 we observed two marked periods. A dry pre-monsoon period (May and June) characterized by a strong drought was present at both sites. Total precipitation in the pre-monsoon period was 106 mm for the deciduous forest and 95 mm for the mixed forest (Table 1a). During monsoon season (July – August) storm events were more recurrent. The deciduous forest had a total of 14 important storm events with intensities that ranged from 18.4 mm d^{-1} to 71.8 mm d^{-1} (Table 2). Its total rainfall (May – August) was 799.8 mm (Table 1a). On the other hand the mixed forest had a total of 12 important storm events during the monsoon season. Its intensities ranged between 18.2 mm d^{-1} and 131.8 mm d^{-1} (Table 2). The total rainfall at this site was 722.8 mm (Table 1a).

In 2014 a failed monsoon season was driving the hydrological processes in both forest sites. Marked periods (dry pre-monsoon and monsoon season) were not present in this year. The total rainfall at the deciduous forest was 220.4 mm (Table 1a). Although storm events were almost absent, one rainfall with major intensity at this site reached 62.4 mm d^{-1} (Table 2). In the mixed forest total rainfall was 197.8 mm. With a few storm events, the rainfall with the highest intensity at this forest was 42.4 mm d^{-1} (Table 2). At both sites the total rainfall represented 27.5% of the total precipitation in the year before.

The occurrence or absence of pronounced monsoon season rainfalls affected total discharge values in both forest sites as shown in Table 1b. The differences between the discharge in the dry pre-monsoon season and monsoon season in 2013 were remarkable. Discharge runoff during the monsoon season in the deciduous forest represented 83% or 95% of the total discharge during the 2013 sampling period at the deciduous or mixed forest, respectively. In 2014 the almost missing monsoon season reduced discharge amounts heavily. Total discharge during 2014 represented less than 1% of the year before. Especially at the mixed forest site discharge runoff was less than a cubic meter per day (Table 1b).

Table 1. Maximum (Max), minimum (Min) and average (Ave) daily (a) input (mm d^{-1}) and (b) discharge runoff (m^3 d^{-1}) data for the investigated forest sub- catchments within the Soyang lake watershed, during the sampling campaigns in 2013 and 2014. Daily values were summed up to obtain total rain input (mm) and discharge runoff (m^3) data and separated for the usually dry pre-monsoon season (May - June) and the usually rainy monsoon season (July and August).

Forest land use		[(a)]Precipitation 2013			Precipitation 2014		
		Dry Season	Monsoon season	Total	Dry Season	Monsoon season	Total
Deciduous	**Total (mm)**	***106.6***	***693.2***	***799.8***	***62.8***	***157.6***	***220.4***
	Min (mm d^{-1})	0.2	1.8		0.2	0.2	
	Max (mm d^{-1})	27.2	71.8		17.4	62.4	
Mixed	**Total (mm)**	***95***	***627.8***	***722.8***	***117.4***	***80.4***	***197.8***
	Min (mm d^{-1})	0.2	0.6		0.2	0.2	
	Max (mm d^{-1})	20.4	131.8		12.2	42.4	
		[(b)]Discharge 2013			Discharge 2014		
Deciduous	**Total (m^3)**	***8.4 x 10^5***	***3.9 x 10^6***	***4.7 x 10^6***	***264.2***	***990***	***1254.1***
	Min (m^3 d^{-1})	1.0 x 10^4	1.8 x 10^4		7.9	16.3	
	Max (mm^3 d^{-1})	4.2 x 10^4	2.4 x 10^6		21.9	58.5	
	Average (mm^3 d^{-1})	2.7 x 10^4	1.5 x 10^5		17.6	22.4	
Mixed	**Total (m^3)**	***2.9 x 10^3***	***7.1 x 10^4***	***7.4 x 10^4***	***33.9 x 10^{-4}***	***18.8 x 10^{-3}***	***22.2 x10^{-3}***
	Min (m^3 d^{-1})	60.8	104.8		24.1 x 10^{-5}	22.2 x 10^{-6}	
	Max (mm^3 d^{-1})	164.2	1.4 x 10^4		58.2 x 10^{-5}	19.9 x 10^{-4}	
	Average (mm^3 d^{-1})	104.8	2.7 x 10^3		48.4 x 10^{-5}	44.9 x 10^{-5}	

3.2 Nitrate concentrations and seasonality of nitrate fluxes

3.2.1 Nitrate in rain

During sampling campaign in 2013 nitrate concentrations in rain ranged between 0.2 and 10 mg L^{-1} and between 0.5 and 15 mg L^{-1} in the deciduous and mixed forest, respectively. The average nitrate concentration in rain was 2.9 ± 2 mg L^{-1} at both forests. In 2014 nitrate concentrations in rain ranged between 1.3 and 18 mg L^{-1} at the deciduous site and between 1.5 and 17 mg L^{-1} at the mixed forest. Mean values of nitrate concentrations were 7.6 ± 5 mg L^{-1} or 6.8 ± 4 mg L^{-1} at the deciduous and mixed site, respectively. Thus, nitrate concentrations in rainfall were by a factor of about three higher in the year with low precipitation. Nonetheless, precipitation amounts were not correlated ($P > 0.050$) with nitrate concentrations, and no seasonality in nitrate concentrations in rainfall was found.

Table 2. Strom events (date) and rainfall intensity (mm d^{-1}) during monsoon season (July - August) for the investigated forest sub-catchments during the sampling campaigns in 2013 and 2014. The storm events with the highest intensity are shown in bold letters.

orm events	*Deciduous*		*Mixed*	
	Date	***ain (mm.d^{-1})***	***Date***	***ain (mm.d^{-1})***
2013	02.07.2013	48.4	02.07.2013	31
	08.07.2013	98	08.07.2013	57
	09.07.2013	23	10.07.2013	30.4
	10.07.2013	28.8	11.07.2013	44.4
	11.07.2013	69.8	12.07.2013	31.8
	12.07.2013	69.8	13.07.2013	18.2
	13.07.2013	27.6	**14.07.2013**	**131.8**
	14.07.2013	**71.8**	15.07.2013	50.4
	15.07.2013	58	18.07.2013	119.4
	18.07.2013	60.6	21.07.2013	20.2
	21.07.2013	24.2	22.07.2013	28.2
	22.07.2013	20.2	23.07.2013	46.8
	23.07.2013	52.8		
	24.07.2013	18.4		
	Deciduous		***Mixed***	
	Date	***ain (mm.d^{-1})***	***Date***	***ain (mm.d^{-1})***
2014	**25.07.2014**	**62.4**	01.07.2014	13.2
	10.08.2014	46.2	25.07.2014	31.8
			31.07.2014	27.2
			10.08.2014	**42.4**

Total rain fluxes and associated nitrogen inputs during the sampling periods of the two investigated years are plotted in Fig. 2 in a multiple line and scatter flux diagram over time. In Table 3 these single data are summarized. Total nitrogen input from nitrate rainfall during the sampling period in 2013 in the two forest sub-catchments was 7.8 or 10.1 kg N_{NO3}^{-} ha^{-1} for the deciduous and mixed site, respectively. In the following year without pronounced monsoon season total nitrogen input from nitrate in rainfall was 4.3 kg N_{NO3}^{-} ha^{-1} or 4.1 kg N_{NO3}^{-} ha^{-1} for the deciduous and mixed forest, respectively. The N_{NO3}^{-} rain input during the monsoon season in 2013 represents 95% or 80% of the total nitrogen from nitrate rainfall during the summer campaign in the deciduous and mixed forest, respectively. In absence of a pronounced monsoon season, the total N_{NO3}^{-} rain input in the summer campaign in 2014 represents 40% of the total nitrogen from nitrate rain input in 2013 in both forests.

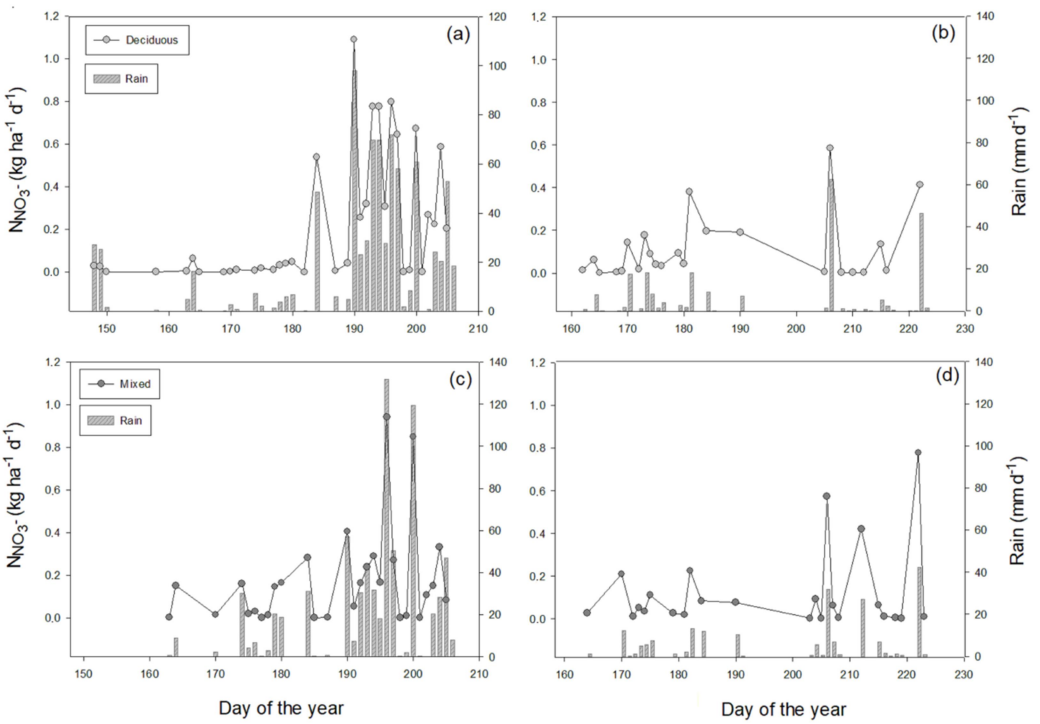

Fig. 2. Nitrogen input from nitrate deposition by rainfall (kg ha^{-1}) measured at the deciduous and mixed forest sub-catchments, temporal distribution and intensity of rainfall events during the sampling campaigns (May to August) in (a and c) 2013 and (b and d) 2014.

In the deciduous forest N_{NO3}^- rain input during the monsoon year 2013 was 2.5 times higher than the total N_{NO3}^- river discharge. In the mixed forest the total N_{NO3}^- rain input and total N_{NO3}^- discharge showed an opposite behavior. N_{NO3}^- rain input represented only 50% of the total N_{NO3}^- river discharge in this year. Thus, in the monsoon year 2013, in contrast to the deciduous forest, the mixed forest did not function as a sink for atmospheric nitrate deposition, but rather as a nitrate source. In 2014 without pronounced monsoon season the N_{NO3}^- rain input was by far lower than the total N_{NO3}^- discharge at both sites. In this particular year both forest sites were acting as a sink for the nitrogen from atmospheric nitrate deposition.

Table 3. Total nitrogen input from nitrate deposition by rainfall separated between deciduous forest, and mixed/deciduous and mixed/coniferous for the campaign in 2013 and 2014, calculated on a hectare basis (kg N_{NO3}^- ha^{-1}) in the investigated forest sub-catchments within the Soyang lake watershed.

Forest sub-catchment nitrogen from nitrate rain input										
Forest land use		***ha***	***2013***				***2014***			
			Total	***Maximum***	***Minimum***	***Mean***	***Total***	***Maximum***	***Minimum***	***Mean***
			N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$	N_{NO3}^-***kg ha*$^{-1}$
Deciduous		38.97	**7.8**	1.0	21.7 x 10^{-5}	0.21	**4.3**	0.6	79.7 x 10^{-5}	0.1
Mixed	***Deciduous***	9.25	4.7	1.1	11.2 x 10^{-4}	0.18	1.8	0.9	24.7 x 10^{-4}	0.1
	Coniferous	6.25	5.4	0.6	76.2 x 10^{-5}	0.16	2.2	0.8	55.4 x 10^{-4}	0.1
	Total	15.5	**10.1**				**4.1**			

3.2.2 Nitrate in stream runoff

During sampling period in 2013, nitrate concentrations in the river discharge ranged between 6.5 mg L^{-1} and 12.5 mg L^{-1} at the deciduous site and between 10.5 mg L^{-1} and 26.7 mg L^{-1} at the mixed forest. The mean values were 8.6 ± 1 mg L^{-1} or 16.2 ± 3 mg L^{-1} for the deciduous and mixed forest respectively. The relationship between discharge and storm events with nitrate concentration in stream runoff was not significantly correlated ($P > 0.050$) in any of the years. During summer in 2014 nitrate concentrations in runoff ranged between 10.9 mg L^{-1} and 14.7 mg L^{-1} in the deciduous forest and between 11.8 mg L^{-1} and 22.8 mg L^{-1} at the mixed site. The nitrate concentrations in river discharge in 2014 were significantly ($P = < 0.001$) higher than in the year before. Thus, the low discharge amounts in 2014 carried higher nitrate concentrations than in the year before.

Total N_{NO3}^- river discharge was higher from the mixed forest than from the deciduous site in both years. During sampling period in the monsoon year 2013 nitrogen from nitrate discharge in the mixed forest was 20.3 kg ha^{-1} and in deciduous forest it was 3.2 kg ha^{-1} (Table 4). In 2014 without pronounced monsoon season N_{NO3}^- discharge was as low as 0.08 kg ha^{-1} or 0.6 kg ha^{-1} for the deciduous and mixed forest, respectively (Table 4). Although during the sampling period in 2014 the nitrogen runoff was only 3% of the total N_{NO3}^- discharge in 2013, in both years N_{NO3}^- river runoff at the mixed forest was between 6 to 7 times higher than at deciduous forest. Fig. 3 shows further details of total N_{NO3}^- river discharge fluxes in a multiple line and scatter flux diagram over time.

Table 4. Total nitrogen discharge runoff separated by forest sub-catchments, during the campaigns in 2013 and 2014 and calculated on a hectare basis (kg N_{NO3}^- ha^{-1}) in the investigated deciduous and mixed forest . Total values for both forest sub-catchments are shown in bold letters. For the mixed forest, values are divided between coniferous and deciduous patches.

Forest sub-catchment nitrogen from nitrate runoff						
Forest land use		**ha**	**2013**			**2014**
			Total	**Dry**	**Monsoon**	
			$_{NO3}^-$kg ha^{-1}	**$_{NO3}^-$kg ha^{-1}**	**$_{NO3}^-$kg ha^{-1}**	**$_{NO3}^-$kg ha^{-1}**
Deciduous		**38.97**	**3.2**	1.8	1.4	**0.08**
Mixed	Deciduous	9.25	8.5	0.2	8.2	0.3
	Coniferous	6.25	11.8	0.3	11.4	0.3
	Total Mixed	**15.5**	**20.3**	0.6	19.7	**0.6**

The marked dry pre-monsoon and monsoon season in 2013 influenced N_{NO3}^- river runoff especially in the mixed forest (Fig. 3c). A great variation of N_{NO3}^- discharge was observed. The N_{NO3}^- river discharge increased with the frequency of rain events. 80% of the nitrogen from nitrate discharge in the mixed forest was lost during the monsoon season. Only 20% of the total N_{NO3}^- river runoff was during the dry pre-monsoon season. A positive correlation between N_{NO3}^- runoff peaks and storm events were found at this site ($P < 0.050$) (Fig. 3). In the deciduous forest such variation could not be observed. Total N_{NO3}^- discharge was equally distributed between pre-monsoon and monsoon season. The more stable nitrate nitrogen runoff from the deciduous forest resulted in a negative correlation ($P > 0.05$) between N_{NO3}^- runoff peaks and rain events (Fig. 3a and e).

In 2014 no seasonality was observed over the sampling period. Although N_{NO3}^- discharge was stable along the sampling campaign in both forests and no correlation between N_{NO3}^- and storm events were found ($P > 0.05$, Fig. 3f and h), we observed small N_{NO3}^- runoff peaks associated to the few rain and small storm events in this year (Fig. 3b and d).

3.3 $\delta^{15}N$ and $\delta^{18}O$ of nitrate input and output

Nitrate $\delta^{15}N$ and $\delta^{18}O$ values in atmospheric input (rain, data from literature) and stream water (own data) are summarized in Table 5. Literature data for nitrate in rainfall in South Korea indicate ranges between -2 ‰ and +14 ‰ for $\delta^{15}N$ and between +25 ‰ and +75 ‰ for $\delta^{18}O$. The $\delta^{15}N_{NO3}^-$ values found in the stream water output ranged between -1.6 ‰ and +3.5 ‰ and between -4.2 ‰ and +6.1 ‰ at the deciduous and mixed forest, respectively. The $\delta^{18}O_{NO3}^-$ values in the deciduous and mixed forest river water were between -1.6 ‰ and +10.6 ‰ and between -4.1 ‰ and +23.7 ‰, respectively. Thus, nitrate $\delta^{15}N$ values in stream water ranged at the lower end or were below the nitrate $\delta^{15}N$ values in precipitation, and nitrate $\delta^{18}O$ values in stream water had a wide range of variation, but were consistently below the nitrate $\delta^{18}O$ values in precipitation. A closer look on the single stream water $\delta^{18}O_{NO3}^-$ values in dependence on the day of sampling (Fig. 4a) or in dependence on rainfall events (Fig. 4b) in the monsoon year 2013 provides clues for the reason of the high stream water $\delta^{18}O_{NO3}^-$ variation. In the dry pre-monsoon period stream water $\delta^{18}O_{NO3}^-$ values ranged between +10.6 and -4.1 ‰ and were pretty similar for the deciduous and the mixed forest site. In the monsoon season stream water $\delta^{18}O_{NO3}^-$ values of the deciduous forest site behaved similar to the pre-monsoon season. However, the majority of the stream water $\delta^{18}O_{NO3}^-$ data from the mixed forest site increased in the monsoon season to values between +15 and +23.7 ‰.

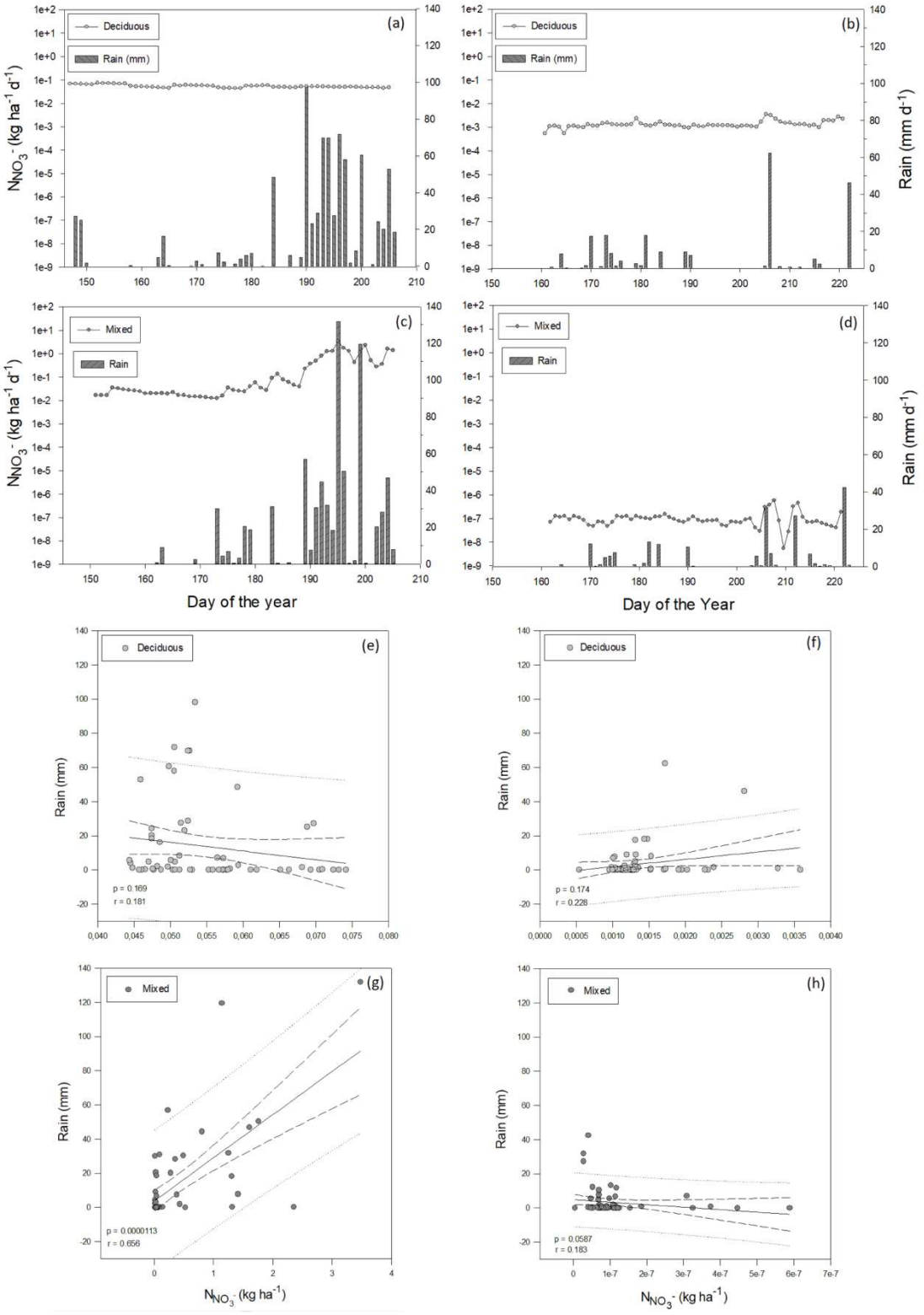

Fig. 3. Temporal distribution of total N_{NO3}^- fluxes (kg ha^{-1} d^{-1}) in discharge runoff measured at the forest sub-catchments, during the sampling campaigns (May to August) in deciduous site (a) 2013 and (b) 2014 and mixed site (c) 2013 and (d) 2014. Correlations between peaks in N_{NO3}^- (kg ha^{-1}) and storm events (mm) at the deciduous forest during monsoon season 2013 (e) and 2014 (f). Correlations between peaks in N_{NO3}^- (kg ha^{-1}) and storm events (mm) at the mixed forest during monsoon season 2013 (g) and 2014 (h).

Table 5. Nitrate $\delta^{15}N$ and $\delta^{18}O$ isotopic composition from atmospheric nitrate deposition (rain) that may influence nitrate discharge runoff in the forest sub-catchments and stream water isotopic composition. [a]Rain atmospheric deposition values were taken from Lee et al. (2008).

Forest sub-catchments							
Isotopic composition		***$\delta^{15}N$***			***$\delta^{18}O$***		
Forest		**Maximum (‰)**	**Minimum (‰)**	**Average (‰)**	**Maximum (‰)**	**Minimum (‰)**	**Average (‰)**
Deciduous	Stream	3.5	-1.6	0.4 ± 1	10.6	-1.6	1.8 ± 3
	Rain[a]	14	-2		75	25	
Mixed	Stream	6.1	-4.2	0.6 ± 2	23.7	-4.1	6.3 ± 7
	Rain[a]	14	-2		75	25	

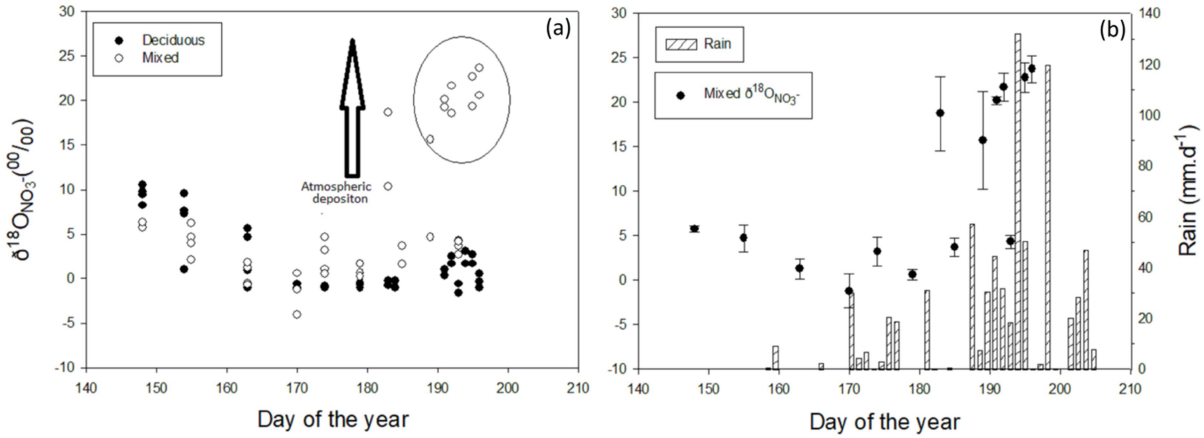

Fig. 4. Temporal distribution of nitrate $\delta^{18}O$ isotopic composition in stream water in the investigated deciduous and mixed forest (a) and temporal distribution in the mean values for nitrate $\delta^{18}O$ in stream water and rainfall events at the mixed forest (b). Arrow represents the direction of the nitrate $\delta^{18}O$ isotope composition in atmospheric deposition (Lee et al. 2008).

3.4 Soil nitrate status

Nitrate concentrations collected in the dry year 2014 along a soil depth gradient (10-60 cm) in the forest soils ranged between 11.6 mg L^{-1} and 26.6 mg L^{-1} and 4.4 mg L^{-1} and 13.1 mg L^{-1} at the deciduous and mixed forest site, respectively (Fig. 5a and b). The lowest values were observed in the mineral soil (50 and 60 cm) of the mixed and of the deciduous forest. The organic layer (0-20cm) had higher nitrate concentrations than the mineral layer in both forests, although in the deciduous forest we observed in general higher nitrate concentrations than in the mixed forest. This difference was highly significant ($P < 0.001$). In each soil depth the pH values of the mixed forest were by about one unit lower than in the deciduous forest (Table 6). This

difference was significant ($P < 0.05$). The mean soil pH value for the mixed forest was 4.4 ± 0.4 and of the deciduous forest 5.35 ± 0.5.

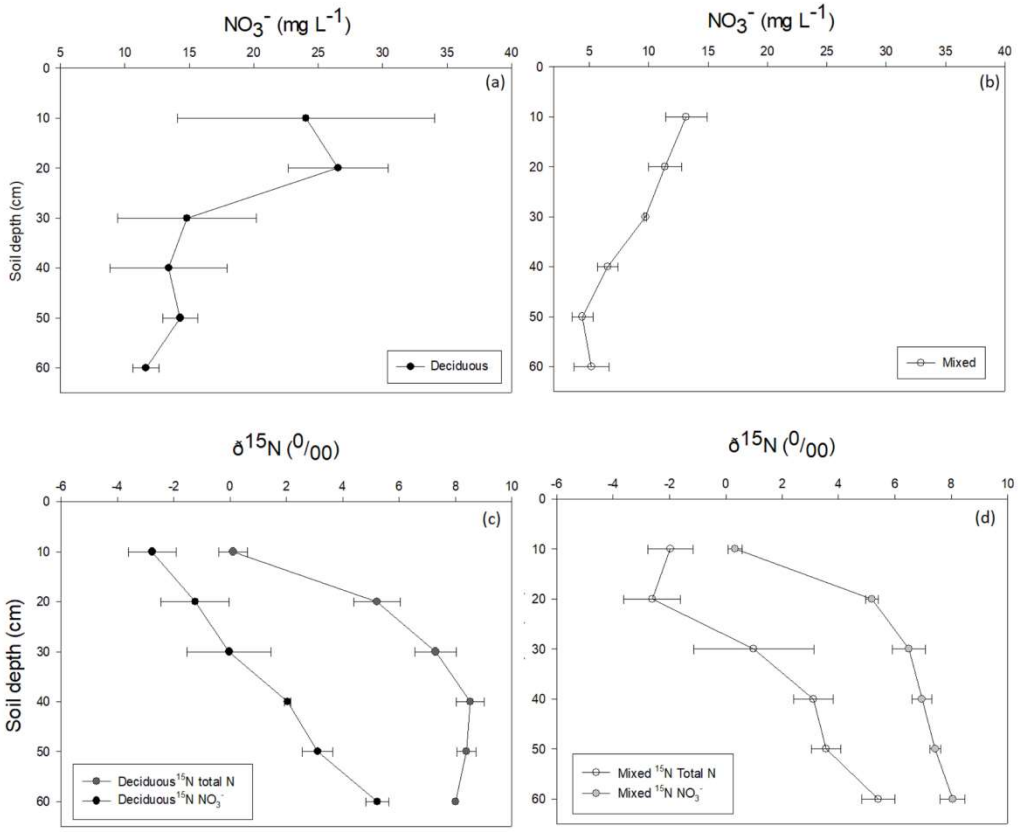

Fig. 5. Nitrate concentrations and $\delta^{15}N$ values of nitrate and total nitrogen (Lee et al. 2016) along a soil depth gradient in the deciduous (a and c) and mixed forest (b and d) at the investigated forest sub-catchments.

Negative and significant correlations ($P < 0.05$) between nitrate concentration and soil depth were found in both forests (Fig. 6a and b). In the mixed forest soil this correlation was stronger ($r = 0.910$) than in the deciduous forest soil ($r = 0.580$).

The $\delta^{15}N_{NO3}^-$ values along the depth profiles ranged from -2.8 ‰ or -2.6 ‰ in the organic layer to +5.2 ‰ or +5.4‰ in mineral soil of the deciduous and mixed forest, respectively (Fig. 5c and d). Robust positive correlations (deciduous $r = 0.924$; mixed $r = 0.887$) were found between $\delta^{15}N_{NO3}^-$ and soil depth at both forest sites ($P < 0.05$; Fig. 6c and d). The $\delta^{15}N_{NO3}^-$ values in identical soil depths were not significantly distinguished between the two forests ($P > 0.05$). However significate differences ($P < 0.05$) were observed between organic and mineral layers in both studied sites.

Significantly negative correlations were found between $\delta^{15}N_{NO3}$- and nitrate concentrations ($P < 0.05$) in both forest soils (Fig. 6e and f). At the mixed forest site this correlation was stronger ($r = 0.805$) than in the deciduous forest ($r = 0.544$). In organic layers δ^{15} N_{NO3}^- values were depleted while nitrate concentrations were simultaneously high, especially in the deciduous forest.

The $\delta^{15}N$ values of soil total nitrogen (literature data from the same forest sites) increased from 0.11 ‰ or 0.32 ‰ in the organic layer to 8.00 ‰ or 8.04 ‰ in the mineral soil of the deciduous and mixed forest, respectively. This increase in $\delta^{15}N$ of soil total nitrogen ran mostly in parallel with our depth gradient in $\delta^{15}N_{NO3}$- for both investigated forest sites (Fig. 5c and d). Soil nitrate from identical positions along the gradient was consistently more depleted in ^{15}N than soil total nitrogen. The difference between $\delta^{15}N$ of soil total nitrogen and $\delta^{15}N_{NO3}$- ranged between a minimum of 2.87 ‰ (organic layer) and a maximum of 7.31 ‰ (30 cm depth) at the deciduous forest site and between a minimum of 2.28 ‰ (organic layer) and a maximum of 7.79 ‰ (20 cm depth) at the mixed forest site.

Table 6. Soil pH values at different soil depths in the investigated deciduous and mixed forest sub-catchments. Mean pH values are shown in bold font for each site.

	Forest soil pH values			
Soil depth (cm)	**Mean Mixed**	**SD Mixed**	**Mean Deciduous**	**SD Deciduous**
10	4.8	0.2	5.7	5.2
20	4.6	0.3	5.8	0.4
30	4.0	0.05	5.1	0.1
40	4.6	0.2	5.1	0.1
50	4.0	0.1	4.9	0.2
60	3.8	0	4.8	0.1
Mean Mixed		**4.4**		
SD mixed		0.4		
Mean Deciduous		**5.35**		
SD Deciduos		0.5		

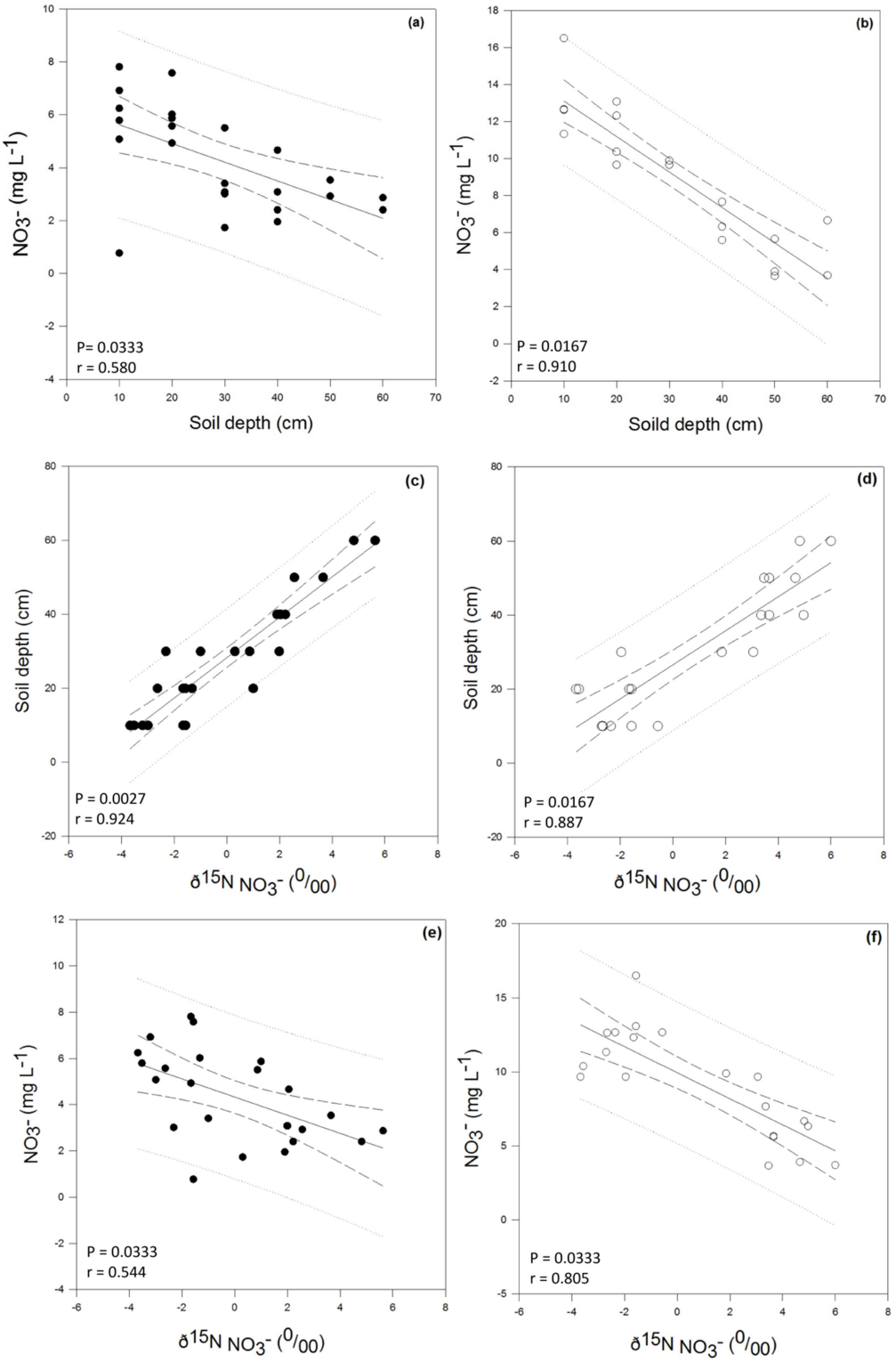

Fig. 6. Correlation between nitrate $\delta^{15}N$ values, nitrate concentrations, and soil depths. Nitrate concentration correlated with soil depth (a and b), nitrate $\delta^{15}N$ values correlated with soil depth (c and d) and nitrate $\delta^{15}N$ values correlated with nitrate concentrations (e and f) at the investigated deciduous and mixed forest.

4. Discussion

4.1 Extremely different monsoon seasons and hydrological responses

East Asian monsoon season and in particular year by year trends of monsoon in South Korea have been studied in several investigations. Temporal distribution in precipitation, rainfall intensities and annual drought breaks in the monsoon season were found to be related to global temperature increases and climate change (Wang et al. 2006; Rajeevan et al. 2008; Ashfaq and Trapp 2009).

Extreme differences in the patterns of the Asian monsoon where observed during the years 2013 and 2014 especially in the northern part of South Korea. These extremely different monsoon seasons clearly influenced the hydrological processes in the studied deciduous and mixed forest sites. The monsoon season in 2013 had rainfall amounts above the eleven years average (Kim et al. 2007), while monsoon season in 2014 failed. In 2014 rainfall amounts were far below the eleven years average (Kim et al. 2007).

Discharges in the studied forests were directly related to the rainfall intensities and amounts in both years. Especially in the monsoon season 2013, a characteristic dry pre-monsoon season drove the very low stream discharge runoff before the monsoon season while discharge increased in parallel with the increase in precipitation and storm events. Several studies have shown that strong monsoon precipitations are the key driver controlling the discharge (Kim et al. 2007; Bartsch et al. 2014; Shope 2016). Although monsoon precipitation plays a major role for discharge runoff, a variety of local conditions influence also the water distribution, like geology, topography, soil water holding capacity and land use (Boluwade and Madramootoo 2013; Radatz et al. 2013).

This influence of monsoon rainfall on discharge fluctuations was not present in 2014 due to the failed monsoon season. Variations in the trends of monsoon rainfalls can represent unpredictable hazards for water quality, but also uncertain changes in the biogeochemical processes that can shift sources of nitrate leaching.

4.2 Seasonality of nitrate input and output at the deciduous and mixed forest site

Nitrate concentrations in rain at the deciduous and mixed forest had an average of 2.7 mg L^{-1} in 2013 and 7.2 mg L^{-1} in 2014. Although these nitrate concentrations in rain were significantly different between years ($P < 0.001$), the results showed no relation ($P > 0.05$) with rainfall or

storm events in any sampling campaign. Nitrate concentrations in rainfall in 2013 were below and in 2014 above the average (6.1 mg L^{-1}) reported for the period 1996 to 2000 for three sites in South Korea (Hong et al. 2002). Like in our investigation, Hong et al. (2002) found increased nitrate concentrations in rain during dry periods and decreased nitrate concentrations during summer monsoon rainfalls. Although we did not find a significant seasonality in nitrate concentrations in rain between dry pre-monsoon and monsoon season in 2013, we found great differences between a year with high monsoon rainfall events (2013) and a year with a monsoon almost completely failed (2014). Even though several local studies have shown decreases of nitrate concentrations in rain (Vet et al. 2013), rain nitrate concentrations registered in South Korean are higher than in Japan and lower than in China (Kaneyasu 1995; Wakamatsu et al. 1996; Sun et al. 1998; Lee et al. 2000; Shimohara et al. 2001; Lü and Tian 2007; Duan et al. 2016).

Total nitrate nitrogen fluxes with rain input were strongly and positively correlated ($P < 0.05$) with the corresponding amount of rain in both years and in both forest sites (Fig. 2). Such a correlation between atmospheric nitrogen wet deposition and amount of monsoon precipitation was also found in other studies in Asia (Liu et al. 2011; Lee et al. 2012; Pan et al. 2012; Yu et al. 2014). Thus, atmospheric N_{NO3-} wet deposition in 2014 despite higher nitrate concentrations was only 40% of the total deposition in 2013, due to the low rainfall of this year.

Especially forests are considered to receive N inputs mainly through wet atmospheric deposition (Aber et al. 2003). The nitrogen additions should be smaller than 2 kg N ha^{-1} yr^{-1} in areas unaffected by industrial sources (Lovett et al. 1982; Aber et al. 1989). Our results showed higher atmospheric nitrogen deposition solely from summer monsoon seasons. Thus, emissions of oxidized nitrogen compounds from local and regional transport and from industrial activities in the 140 km northeast of our forest sites located 20 million metropolis Seoul are the most probable origin of the nitrate deposition observed at our forest sites.

Aber et al. (1989) suggested that forests saturated by nitrogen due to atmospheric nitrogen deposition may become sources of nitrogen rather than sinks. With respect to this suggestion the here investigated two forests behaved different.

As hypothesized nitrate concentrations in discharge runoff in the mixed forest were higher than in the deciduous forest in both years. In general, different tree species have distinct capacities for nitrate assimilation (Gebauer and Schulze 1997). The nitrate assimilation capacity of conifers per unit of biomass is by a factor of 2 to 10 lower than the nitrate assimilation capacity of a variety

of broadleaf species (Gebauer and Schulze 1997). Conifers prefer ammonium over nitrate as nitrogen source (Buchmann et al. 1995; Gebauer et al. 2000) and create with their litterfall soil pH values lower than in the soils of broadleaf forests under otherwise identical conditions. The lower pH values in the soil of our mixed forest site compared to the broadleaf forest site are in agreement with this general trend. More acidic soil pH values reduce microbial nitrification and thus, ammonium becomes dominant over nitrate in coniferous forest soils (Buchmann et al. 1995; Gebauer et al. 2000). This preference for ammonium makes coniferous forests under conditions of continuous atmospheric nitrate deposition more prone for nitrate leaching than broadleaf forests. The presence of broadleaf trees in our mixed forest site was obviously not sufficient to prevent the observed increase in nitrate runoff.

For the further analysis of the results in N_{NO3-} discharge runoff at our forest sites we have to consider, in addition to the tree species composition, the influence of the nitrogen atmospheric deposition and monsoon influence on the biogeochemical processes and retention efficiencies in each forest. During the summer in 2014 N_{NO3-} river flux was correlated with discharge runoff at both sites. The lack of rainfall and low discharge lead to lower N_{NO3-} in the river discharge. In general, there was lower N_{NO3-} discharge than atmospheric N_{NO3-} input. Although both forests acted as sinks for N_{NO3-} driven by the failed monsoon rainfall in this year, still the mixed forest had 6 to 7 times higher N_{NO3-} output into the stream water than the deciduous forest. Higher atmospheric nitrate deposition together with heavy rainfalls in the monsoon season in 2013 turned the mixed forest to a nitrate source with higher nitrate output than input while the broadleaf forest continued to serve as a nitrate sink despite of increased nitrate runoff.

4.3 Nitrate source identification

If we assume that 70% of the atmospheric nitrogen deposition occurs with rainfall (Lee 2000), we might expect in the first instance nitrogen from atmospheric nitrate deposition to be a major nitrate source in the river discharge. A comparison of the isotopic composition of nitrate input and output provides a first clue to check whether this assumption holds true. The isotopic composition of nitrate can, furthermore, provide information on biogeochemical nitrate transformation processes in forests like soil microbial nitrification and denitrification (Amberger and Schmidt 1987; Revesz et al. 1997; Silva et al. 2000). Our finding of $\delta^{15}N_{NO3}^-$ values in stream water at the lower end or below the $\delta^{15}N_{NO3}^-$ values in precipitation and of $\delta^{18}O_{NO3}^-$ values in stream water consistently below the $\delta^{18}O_{NO3}^-$ values in precipitation (Lee et al. 2008) indicates that directly leached nitrate from atmospheric deposition was mostly not the dominant

contributor to the stream water nitrate. Increases in stream water $\delta^{18}O_{NO3}^-$ values towards $\delta^{18}O_{NO3}^-$ values in atmospheric deposition on heavy monsoon rainfall events and only observed at the mixed forest site indicate only for the monsoon period and only for the mixed forest a major direct contribution of rainfall nitrate to the stream runoff nitrate (Durka et al. 1994; Crayosky et al. 1999; Curtis et al. 2011). In order to test this conclusion and to identify alternative sources for the nitrate in stream runoff we compare in Fig. 7 our stream runoff $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ data with $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ values as to be expected theoretically for microbial nitrification at these particular sites: $\delta^{15}N_{NO3}^-$ between -6 and +6 ‰ and $\delta^{18}O_{NO3}^-$ between -1.6 and +5.9 ‰ (Durka et al. 1994; Wassenaar 1995; Kendall and McDonnell 1998). For the deciduous forest site only very few stream runoff $\delta^{15}N_{NO3}^-$ and $\delta^{18}O_{NO3}^-$ data exclusively from the pre-monsoon season do not fall into the range of nitrate isotope abundances as to be expected for nitrate from microbial nitrification. Thus, for the deciduous forest site nitrate from soil microbial nitrification appears as major contributor to the stream runoff nitrate. For the mixed forest site a separation between pre-monsoon and monsoon sampling is essential. While stream runoff nitrate isotope data in the pre-monsoon season indicate exclusively soil microbial nitrification as nitrate source, in the monsoon season nitrate from two sources, microbial nitrification and direct leaching of atmospheric deposition, contribute to the stream runoff nitrate of the mixed forest site.

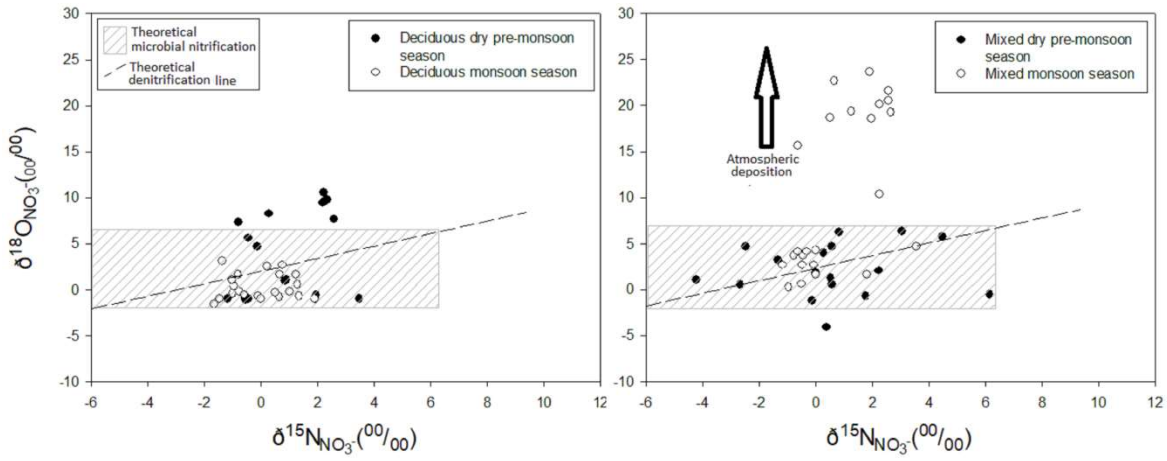

Fig. 7. Nitrate $\delta^{15}N$ and $\delta^{18}O$ values in stream water collected in 2013 plotted together with a calculated theoretical microbial nitrification (lined box) and denitrification (dotted line) in the investigated deciduous and mixed forest during growing season. Arrow represent the direction of the nitrate $\delta^{18}O$ isotope composition in atmospheric deposition (Lee et al. 2008).

4.4 Soil nitrate status

Higher nitrate concentrations as observed for the soil along depth profiles in parallel with higher soil pH values at the deciduous forest site indicate most probably higher microbial mineralization and nitrification rates (Gebauer and Schulze 1997; Pardo et al. 2007) or better retention capacities of atmospheric nitrate deposition due to a higher C:N ratio (Lee et al. 2016) than at the mixed forest site. Adams et al. (2004) have used C:N ratios to predict retention capacities of nitrate in the soil, and it has been related with nitrification rates as well. Pronounced depth gradients in $\delta^{15}N$ of soil total nitrogen as reported by Lee et al. (2016) for the two sites of this investigation are a characteristic general feature of temperate forest soils (Nadelhoffer and Fry 1988; Gebauer and Schulze 1991; Gebauer et al. 1994; Högberg 1997; Pardo et al. 2007). They originate from isotope fractionations during microbial mineralization and nitrification and lead to decreasing soil total nitrogen concentrations with increasing depth in the profile. Based on this knowledge Nadelhoffer and Fry (1994) developed a conceptual model postulating that nitrate from microbial mineralization and nitrification follows in its isotopic composition the soil total nitrogen isotope gradient, i.e. nitrate from microbial nitrification in the organic layer is more depleted in ^{15}N than nitrate from microbial nitrification in the mineral soil. The model furthermore postulated higher nitrate concentrations from more pronounced nitrification in the organic layer and less nitrification and thus, lower nitrate concentrations in the mineral soil. To our knowledge this conceptual model has never been confirmed under field conditions. Here we show that, indeed, $\delta^{15}N_{NO3}^-$ in soil solution follows the same depth gradient as $\delta^{15}N$ of soil total nitrogen. Furthermore, nitrate concentrations in the soil solution decreased with increasing depth indicating lower nitrification in the mineral soil than in the organic layer. This finding of characteristic nitrate isotope depth gradients could probably only be realized in a dry monsoon season as in 2014. Otherwise soil water movement due to frequent rainfall would have interfered with gradients built up by biogeochemical processes, like microbial nitrification.

5. Conclusion

Our results suggest that forest sub-catchments within the Soyang lake watershed in South Korea are under the influence of atmospheric nitrate deposition especially in periods of heavy monsoon rainfall. Although the main nitrate source in both forest river waters was microbial nitrification, the influence of wet atmospheric nitrate deposition played an important role especially in the mixed forest, where it directly contributed to the nitrate in river runoff and turned this forest to a nitrate source after the onset of a heavy monsoon season. The most probable reason for the lower

nitrate retention capacity of the mixed forest is the lower nitrate assimilation capacity of conifers compared to broadleaf trees.

Nonetheless, atmospheric nitrate deposition influenced both forests, because nitrate was the compound with the higher percentage in the discharge water than any other nitrogen component (Lee et al. 2016) and even though it was not a source for the river water at the deciduous forest most likely affected its internal nitrogen cycling.

Soil nitrate isotopes ($\delta^{15}N_{NO3}^-$) along soil depth profiles showed gradients corresponding to what has been observed for soil total nitrogen $\delta^{15}N$ by other studies (Nadelhoffer and Fry 1988; Gebauer and Schulze 1991; Gebauer et al. 1994; Högberg et al. 1996; Sah and Brumme 2003), but with an offset towards more negative $\delta^{15}N$ values. The $\delta^{15}N_{NO3}^-$ depth gradients of this investigation confirm for the first time under field conditions the conceptual model considerations by Nadelhoffer and Fry (1994) on the mechanisms and the isotope fractionation of microbial nitrogen mineralization and nitrification along depth gradients in forest soils.

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Chapter 4

Relationship between nitrogen isotope ratios of NO_3^- and N_2O in vertical porewater profiles through a polluted rain-fed peat bog (Ore Mts., Central Europe)

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Abstract

Assessments of N_2O production and consumption in waterlogged soils are needed for the formulation of efficient mitigation strategies. We report a combination of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N\text{-}N_2O$ values along vertical porewater profiles in an ombrotrophic, high-elevation peat bog in the Czech Republic (Central Europe). Our objective was to use natural-abundance isotopes to distinguish between N_2O diffusion in pore water, N_2O production from NO_3^- *via* denitrification, and N_2O consumption *via* further reduction to N_2, accompanied by a loss of warming potential. Atmospheric N input into the peat bog was isotopically fingerprinted by monthly monitoring of wet deposition between January 2016 and May 2017. Runoff export was analyzed over the same period of time. Nitrate-N in runoff was isotopically heavier than NO_3^--N in atmospheric deposition (mean $\delta^{15}N$ values of -2.7 and -6.3 ‰, respectively), indicating export of secondary, organically cycled, residual nitrate. Nitrate-N in pore water was identical to atmospheric deposition at a depth of 10-20 cm, isotopically very light at a depth of 30 cm ($\delta^{15}N$ of -9.5 ‰), and identical to runoff at a depth of 60 cm. Nitrous oxide concentrations in the atmosphere were nearly 20 % higher than in peat pore water gas, suggesting that the wetland served as a sink for air-borne N_2O, rather than a N_2O source. Within the vertical porewater profile, nearly constant N_2O concentrations contrasted with a clear-cut shift toward higher $\delta^{15}N\text{-}N_2O$ value upcore (from -5.0 to 2 ‰). In the 60-30 cm depth interval, there was a strong negative correlation between the $\delta^{15}N$ values of nitrate and nitrous oxide. Because reduction of NO_3^- to N_2O is associated with an isotope fractionation toward isotopically lighter N in the product, the found negative N isotope correlation could not be explained by a single denitrification step. We suggest that the relatively high-$\delta^{15}N$ values of nitrate in the deepest peat layer reflected higher rates of NO_3^- reduction, compared to the 30-cm depth, and that the progressively heavier N_2O-N upcore corresponded to residual N_2O following partial reduction to N_2, along with an increasing proportion of atmospheric N_2O in the pore water.

Keywords: nitrate, nitrous oxide, isotopes, peat bog, *Sphagnum*, denitrification

1. Introduction

Since the beginning of the Industrial Revolution, tropospheric concentrations of nitrous oxide (N_2O), the third most important greenhouse, have increased by nearly 20 % (Heil et al., 2014). Soils contribute more than 50 % of global N_2O emissions (IPCC, 2014). Freshwater wetlands store as much as 16 % of total soil nitrogen (Wieder and Vitt, 2006), and minerotrophic fens substantially contribute to biogenic N_2O emissions (Goldberg et al., 2010). In the biosphere, N_2O is mainly produced by nitrification and denitrification (Reddy et al., 1989, Wrage et al., 2001, Zhu et al., 2013). During denitrification, the more widespread of these two processes, nitrate (NO_3^-) or nitrite (NO_2^-) are reduced to NO, N_2O and N_2 (Tieddje, 1988). The two resulting greenhouse gases, NO and N_2O, differ in their atmospheric lifetime; whereas NO is destroyed within hours after emission, the lifetime of N_2O in the atmosphere exceeds 100 years (Frolking et al., 2011). Prior to emission from a wet soil, however, N_2O can be rapidly reduced to N_2, a gas with no warming potential (Palmer et al., 2016). The balance between N_2O production, emission and biological cycling in the soil is controlled by the availability of the NO_3^- substrate and carbon skeletons as electron donors, enzymatic activity of the denitrifying community, and diffusion conditions (Morley and Baggs, 2010, Hill et al., 2016, Berger et al., 2017). Anoxic conditions are needed for microbial respiratory NO_3^- reduction (Knowles, 1982). In dry conditions, which occur more frequently in an era of climatic warming, soils can switch from being an N_2O source to an N_2O sink (Chapuis-Lardy et al., 2007, Goldberg and Gebauer, 2009). It is currently debated to what extent scavenging of air-borne N_2O by soil microorganisms generates a major flux on an annual basis, but this research avenue can clearly contribute to clarifying the current imbalance in global N_2O budgets (Billings, 2008). The nearly 30 % discrepancy between the known global N_2O sources and sinks could be partly explained by an underestimation of N_2O sinks in terrestrial ecosystems (Limpens et al., 2006).

A quantitative assessment of N_2O production and consumption rates in soils under a variety of environmental conditions is needed for efficient N_2O mitigation strategies (Francez et al., 2011, Tauchnitz et al., 2015, Manninen et al., 2016). Sources and sinks of various species of reactive nitrogen (N_r) in soils can be localized, and sometimes also quantified, by measurements of $^{15}N/^{14}N$ isotope ratios (Nadelhoffer and Fry, 1988). Isotope composition of N in both natural-abundance, and ^{15}N-tracer studies, is expressed in the $\delta^{15}N$ notation (*see* Methods section for definition). Several studies have isotopically fingerprinted N pools and

fluxes in wetlands (Bragazza et al., 2005, Inglett et al., 2007, Esmeijer-Liu et al., 2012). In many developed countries, atmospheric deposition of N_r onto wetlands is dominated by anthropogenic nitrate and anthropogenic ammonium (NH_4^+). Nitrate, originating mainly from traffic and industry, usually contains isotopically heavier N, compared to predominantly agricultural ammonium (Harrison et al., 2000; Felix et al., 2015, 2017). Nitrate N can be both isotopically heavier and lighter than atmospheric N_2 that serves as a standard for mass spectrometry ($\delta^{15}N_{N2}$ = 0.0 ‰). $\delta^{15}N$ values of ammonium are usually negative (Bauer et al., 2000). In ombrotrophic (rain-fed) peat bogs, the $\delta^{15}N$ value of living *Sphagnum* is sometimes shifted relative to mass-weighted $\delta^{15}N$ value of rainfall, indicating microbial N-fixation (Vile et al., 2014, Novak et al., 2016). Vertical peat profiles often exhibit a downcore shift to isotopically heavier N (*i.e.,* to higher $\delta^{15}N$ values), resulting from preferential mineralization and export of the light isotope ^{14}N from deeper and older peat layers (Novak et al., 1999, 2015, Kohzu et al., 2003). Within-bog N cycling and/or N_2O production have been isotopically studied by ^{15}N additions *via* soluble N salts or $^{15}N_2$ gas (Li and Vitt 1997; Franzes and Loiseau 1999; Williams et al. 1999, Nordbakken et al. 2003; Blodau et al. 2006; Xing et al. 2011; Fritz et al. 2014; Zajac and Blodau 2016). Production of N_2O by denitrification is characterized by a large N-isotope shift toward isotopically lighter product (Goldberg et al., 2008). The residual NO_3^--N is progressively enriched in the heavier isotope ^{15}N. Currently available methodologies do not permit direct measurements of the $\delta^{15}N$ signature of N_2O emitted from waterlogged and aerated/rewetted soils because extremely long sampling times would be required. Instead, recent studies have provided insights into N_2O production/consumption by measuring $\delta^{15}N$ values of N_2O dissolved in peat bog porewater (Goldberg et al., 2008, 2010, Novak et al., 2015). None of these studies simultaneously analyzed N isotope composition of co-existing NO_3^- and N_2O in the porewater. Yet, complementary data from such an isotope analysis could help to distinguish between N_2O production from NO_3^- by denitrification, N_2O consumption by reduction to N_2, and scavenging of atmospheric N_2O by soil microorganisms along a concentration gradient. Our current study was designed to fill this gap.

We report vertical trends in $\delta^{15}N$ values of porewater NO_3^- and N_2O in a mountain-top peat bog situated in an industrial part of the Czech Republic. Nitrogen isotope data were collected from six different peat depths using a well-replicated design (n = 6 per depth). Vertical trends in NO_3^- and N_2O concentrations in peat porewater were also measured. Additionally, we

isotopically fingerprinted N_r of atmospheric deposition in the growing and dormant season, and determined the $\delta^{15}N$ value of air-borne N_2O. Porewater dynamics were studied by analyzing the isotope composition of oxygen ($\delta^{18}O$-H_2O). Our objective was to determine whether the cycling of both co-existing N species in porewater, NO_3^- and N_2O, was coupled through denitrification, or de-coupled as a result of microbial scavenging of atmospheric N_2O. We hypothesized that coupling of the two coexisting N species would be manifested by a correlation in their $\delta^{15}N$ values.

2. Materials and methods

2.1. Study site

The intact, ombrotrophic peat bog Brumiste (BR; 17 ha; Fig. 1; Tab. 1) is located on a mountain plateau of the Ore Mts. (Erzgebirge, Krusne hory) in the northwestern Czech Republic, Central Europe. The bog's elevation is 930 m, and long-term annual precipitation averages 1080 mm. The bedrock is formed by two-mica granite, the peat depth is 2 m, and the bog's age is estimated to be less than 4,000 years (Dohnal, 1965). The unforested southern part of the bog is nearly 100 % *Sphagnum* covered, with a lawn habitat predominating over hummock/hollows microtopography. The wettest segment with a 2-ha permanent pond is situated in the center, separated from the open southern part by dense, 2.5-m high dwarf-pine dominated vegetation. The area is drained by a small stream (< 0.3 L s^{-1}) to the south (Fig. 1b). The entire wetland is surrounded by mature stands of Norway spruce which were moderately affected by acid rain (*ca.* 1970-1995), manifested by crown thinning and Mg deficiency. The bog is located 30 km upwind from a cluster of 11 coal-burning power plants that were a major source of acidifying SO_2 and NO_x gases. Desulphurization units in these power plants were installed between 1994 and 1996, and emissions of reactive sulfur in the Czech Republic sharply decreased thereafter. Emissions of reactive N also decreased, primarily a result of lower electricity output, accompanying a nation-wide departure from heavy industry following the demise of Communism in 1989. In the past, BR was affected also by transboundary air pollution, originating from obsolete Soviet-style coal-burning power stations in southeastern Germany and southern Poland.

Chemistry of BR surface bog water is given in Tab. 2, bog water pH fluctuates around 4.2. Peat density at BR is between 0.2 and 0.6 g cm^{-3}, increasing downcore; ash content is less than 4 wt. %. Bohdalkova et al. (2013) measured methane emissions from BR. During the growing season, methane emissions reached 260 mg m^{-2}. Novak et al. (2015) studied N cycling at VJ, a similar rain-fed bog situated 4 km west of BR, showing that elevated N deposition in the peak acid rain years caused vertical mobility of buried N, its leaching and export from the peat profile (*cf.,* Lamers et al., 2000).

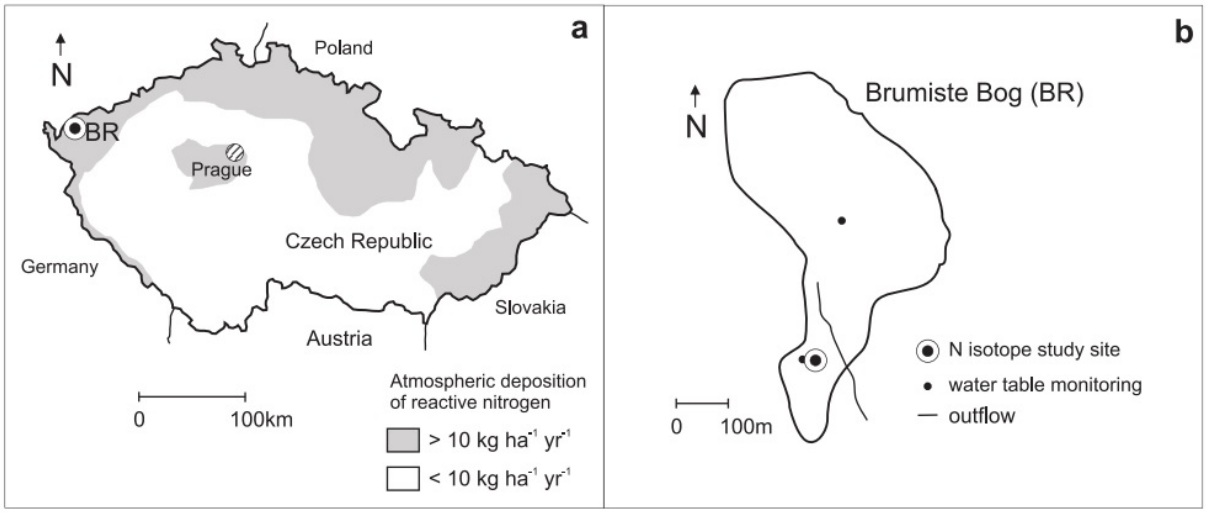


Fig. 1. Study site location. (a) The Brumiste Bog (BR) is situated 20 km west of the "Black Triangle" region near the state border between the Czech Republic, Poland and Germany where, due to industrial acid rain, spruce died back on a territory of 1000 km^2 between 1975-1996. (b) The N isotope study was conducted in a *Sphagnum* lawn extending over the southern tip of BR (large circle); small solid circles mark sites where water table level was monitored by Bohdalkova et al. (2013). Water table data are given in Fig. 7.

Table 1. Study site characteristics.

Site	Brumiste (BR), Czech Republic
Location	50°24´28N, 12°36´40E
Elevation (m a.s.l.)	930
Annual precipitation (mm)	1080
Mean annual temperature (°C)	04. Mai
Bedrock	granite
Bog area (ha)	17
Peat depth (cm)	200
Vegetation	*Sphagnum fallax, Sphagnum papillosum, Polytrichum commune, Eriophorum angustifolium, Carex nigra*

Table 2. Chemistry of Brumiste (BR) bog water, number of samples n = 8 (Bohdalkova et al., 2013).

Site	Mg^{2+} mg L^{-1}	Ca^{2+} mg L^{-1}	Na^{+} mg L^{-1}	K^{+} mg L^{-1}	Fe_{tot} mg L^{-1}	NH_4^{+} mg L^{-1}	NO_3^{-} mg L^{-1}	SO_4^{2-} mg L^{-1}	TOC mg L^{-1}	pH
BR	227 ± 158	722 ± 602	862 ± 374	741 ± 774	591 ± 849	0.04 ± 0.03	0.3 ± 0.3	5.9 ± 6.2	12.3 ± 5.2	4.2 ± 0.2

2.2. Sampling

Three vertical peat cores, 10-cm in diameter, 40-cm long, were collected in the summer of 2014 near the stream draining BR (Fig. 1b). The peat cores were used to determine N concentrations in 2-cm thick vertical peat sections. Monthly monitoring of N concentration and isotope composition in atmospheric deposition and runoff started in January 2016 and ended in May 2017. Three polyethylene (PE) rain collectors, 12-cm in diameter, placed 1.5 m above bog surface, were used to collect open-area precipitation (bulk deposition). The rain collectors were installed in a triangle, five meters apart. For the winter, the rain collectors were replaced with buckets, 35-cm in diameter, to collect snow. Spruce canopy throughfall was collected also by three rain collectors in a 5 x 5 x 5 m arrangement. A 1-L sample of surface runoff was taken once a month. All precipitation and runoff samples were taken to the laboratory, and kept at 4 $^{\circ}$C. Bog porewater and gas samples for N and O isotope analysis were taken in the summer of 2017, 40-200 m from the peat coring and rainfall sampling sites.

N_2O gas samplers

On May 29, 2017, six gas-sampler cylinders were installed in a circle at distances between 2.5 and 3 m to collect soil gas from the peat bog along a depth gradient (Fig. 10 in the Chapter 1: Extended Summary). Each sampler consisted of a 60 cm long PVC cylinder divided in six compartments, 10 cm in length (ID 70 mm; OD 79 mm). Each compartment was perforated by drill holes (diameter of 5 mm) in a 2.5-cm wide band in its center. In the interior of each compartment, a 5 m highly gas-permeable silicone tube collected dissolved gas from each depth (10-60 cm). Each silicone tube was connected to gas-impermeable polyurethane (PUR) tubing that reached the soil surface (ID 1.8 mm; OD 3 mm). At the end of each PUR tube, a plastic stopcock (Luer Lock, Value Plastics, Fort Collins, CO, USA)

was used to connect the device to glass sample storage bottles. Both ends of the main cylinder were sealed. For more details *see* Goldberg et al. (2008).

NO_3^- water samplers

Thirty six suction ceramic cups were installed to collect water samples from the peat bog at six different depths (10-60 cm). Six cups were located at a 1-m distance from each gas sampler (Fig. 10, Chapter 1: Extended Summary). The first cup was installed 10 cm below bog surface, the second cup 20 cm below bog surface, *etc.,* until reaching the 60 cm depth. Each cup was made of P80 ceramic material (porosity 48 vol. %, maximum pore size 1µm; length 7 cm; ID 10 mm; OD 19 mm; CeramTec GmbH, Marktredwitz, Germany) with a PVC tube long enough to reach the required peat depth. Inside the PVC tube, a silicone tube connected the ceramic cup with 2-L plastic bottles placed on the soil surface where the sample was collected. The top of the suction cup was sealed. To collect samples, all suction cups were connected to a vacuum device which allowed the solution from each cup to be transported by underpressure to the bottles. The equipment was linked to a computer control system (Electronic Technical Center, University of Bayreuth), which kept a nearly constant underpressure (HS260P-30 Black Swan, Hanover Solar GmbH, Germany). For more details *see* Göttlein et al. (1996), Göttlein and Matzner (1997).

N_2O gas sampling

Peat porewater gas samples were taken on June 22th, 2017, 24 days after gas sampler installation. Gas samples were collected through the PUR tube connected in one end to an evacuated 100-mL glass bottle and in the other end to an air bag filled with N_2 gas at ambient pressure. The gas sample volume extracted from the compartments at different depths was replaced by N_2 from the attached bag. Ambient air samples (n = 6) were collected on the same sampling date approximately 2 m above the moss surface. Before the sampling, the glass bottles were first flushed with N_2 and then evacuated with a vacuum pump (KNF Neuberger N026.3AN.18, Freiburg, Germany). The N_2O sampling day was preceded by a short very dry period that made the water table drawdown to reach 15 cm below the surface.

NO_3^- water sampling

The vacuum device was activated on June 19, 2017, and operated continuously for the next five days. A minimum volume of 1 L was needed for the laboratory analysis of each porewater sample, therefore we had to wait one day more after N_2O sampling until the volume of each porewater sample became sufficient. The above mentioned dry period influenced the porewater sampling, making the suction pressure rise up to levels normally used to extract water from a 2-m depth (200 to 230 hPa). Between the N_2O and NO_3^- porewater sampling days (*i.e.,* from June 22 to June 23), a storm event turned the peat bog from superficially dry to water-saturated. The water table drawdown after the storm reached about 5 cm below surface. In all, 36 N_2O and 36 NO_3^- samples were collected from six replicates at six different depths.

2.3. Analysis

Substrate from each 2-cm peat core segment was dried at 60 °C and homogenized. A 10-mg aliquot of each sample was placed in a tin capsule and analyzed for N concentration in a Fisons 1108 Elemental Analyzer. The combustion temperature was 1040 °C, and the reproducibility of the N concentration analysis was 1.0 %. Samples of atmospheric deposition and runoff were analyzed for NH_4^+ concentrations by spectrophotometry (Perkin-Elmer 200 Hitachi, 2 SD of 4.4 %), and for NO_3^- concentrations by liquid chromatography (Knauer 1000, 2 SD of 3.8 %). For N isotope analysis, 500 mL of atmospheric deposition or peat porewater were concentrated on Dowex 50W and Dowex 1 x cation and anion exchange resins, and separated into NH_4^+ and NO_3^-. Solution aliquots were made alkaline with MgO and steam-distilled into a small excess of diluted H_2SO_4 (Bremner, 1965). Prior to distillation, Devardas alloy was added for NO_3^- analysis. The resulting ammonium sulfate was dried and analyzed for N isotope ratios. The Fissons 1108 analyzer was connected to a Finnigan MAT 251 mass spectrometer (Bremen, Germany) to measure the N isotope composition. The $^{15}N/^{14}N$ isotope ratios were expressed in the $\delta^{15}N$ notation as a relative ‰ deviation from an agreed-on standard (atmospheric N_2). The 2 SD reproducibility for N isotopes in water was 0.2 ‰.

The porewater gas samples from different peat depths were analyzed for N_2O concentration and N isotope abundance ratios. We used a gas chromatograph–isotope ratio mass

spectrometer coupling with a pre-GC concentration device (PreCon-GC-IRMS) described by Brand (1995; Delta V plus, Thermo Fisher Scientific, Bremen, Germany; GC 5890 series II, Hewlett-Packard, Wilmington, USA; Pre-Con Finnigan MAT, Bremen, Germany). As a laboratory standard, N_2O gas (99.997 %, Reißner, Lichtenfels, Germany) was used, previously calibrated with N_2 and N_2O reference gas. The internal reproducibility of the system was typically ± 0.15 ‰. N_2O concentrations were calculated from the volume of the gas samples and the peak area on m/z 44 using a calibration curve. For further details *see* Goldberg et al. (2008) and Berger et al. (2013).

Laser absorption spectroscopy was used for the determination of oxygen stable isotope ratios in peat pore water. Oxygen isotope analyses of H_2O were performed by off-axis integrated cavity output spectroscopy (OA-ICOS; Liquid Water Isotope Analyser, Model 3000, LGR Inc., Mountain View, Ca, U.S.A.). One µL of water was injected through a port heated to 80°C. The vapour was transported into a pre-evacuated cavity and analyzed for the $^{18}O/^{16}O$ ratio. The $^{18}O/^{16}O$ isotope ratios were expressed in the $\delta^{18}O$ notation as a relative ‰ deviation from an agreed-on standard (V-SMOW). The 2 SD reproducibility for O isotopes in water samples was 0.3 ‰.

Statistical analysis was performed using the R software, version 3.4.3 (R Core Team, 2017). The results for vertically stratified variables are based on one-way analysis of variance (ANOVA) complemented by Tukey's multiple comparison. Time-series of input/output $\delta^{15}N$ values were analyzed using two-way ANOVA adjusted for possible effect of time and possible effect of multiple comparisons. The correlation coefficient between $\delta^{15}N$ values of NO_3^- and N_2O was calculated by the least squares method, and the related *p*-value was based on a one-sided test toward negative correlation.

3. Results

3.1. Atmospheric input and runoff of reactive nitrogen

Maximum NO_3^- concentrations in open-area precipitation and runoff were 7.9 and 8.0 mg L^{-1}, respectively; both recorded in mid-spring, about one month after the snowmelt (Tab. 3). The mean NO_3^- concentrations in open-area precipitation and runoff were similar (1.9 ± 0.6

Table 3. Concentration and $\delta^{15}N$ values of ammonium (NH_4^+) and nitrate (NO_3^-) in atmospheric deposition and runoff, Brumiste Bog (BR), Ore Mountains, Czech Republic.

	Open-area precipitation				Canopy throughfall				Runoff			
	NH_4^+		NO_3^-		NH_4^+		NO_3^-		NH_4^+		NO_3^-	
Sampling date	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**	**conc. (mg L^{-1})**	**$\delta^{15}N$ (‰)**
January 25, 2016	1.58	-9.1	3.99	-6.7								
February 9, 2016	0.61	-7.8	3.43	-2.7								
March 9, 2016	0.71	-9.2	0.40	-7.3					0.11	0.5	0.40	-1.2
April 6, 2016	1.62	-1.9	3.10	-2.6					0.08	-3.0	0.21	-4.6
May 10, 2016	1.65	-2.4	0.44	-7.8					0.31	0.3	0.44	-2.4
June 9, 2016	0.06		0.00	-6.3					0.28	0.1	0.89	-2.9
July 13, 2016	0.18		0.00	0.8					0.31	0.6	0.00	0.7
August 4, 2016	0.81	-3.8	0.00	-6.7					0.05	-5.1	0.33	-3.9
September 6, 2016	0.51	-5.9	0.44	-7.8					0.05	0-1	0.00	-2.5
October 6, 2016	0.05	-3.1	0.44						0.05	-8.4	0.00	-8.3
November 7, 2016	0.15	-4.2	0.00	-7.4					0.13	0.2	0.00	-1.6
December 6, 2016	0.17	-4.9	0.00	-7.3					0.12	3.0	0.00	-0.6
January 9, 2017	0.30	-8.9	2.21	-8.9	0.13	-4.1	0.00	-4.7				
February 8, 2017	0.45	-7.8	3.54	-5.1	0.09	-8.6	3.99	-4.8	0.15	0.1	0.44	-2.3
March 8, 2017	0.36	-15.5	3.10	-11.7	0.33	-8.2	3.99	-3.7	0.09	-9.2	0.54	-2.4
April 6, 2017	1.43	-8.3	7.9	-6.3	0.18	-9.5	0.00	-8.1	0.40	-11.1	0.76	-7.0
May 15, 2017						-6.6	9.74	-4.0	0.24	-3.4	0.97	0.6

and 1.6 ± 0.7 mg L^{-1}, respectively). In contrast, the mean NH_4^+ concentration in runoff (0.17 ± 0.03 mg L^{-1}) was four times lower, compared to open-area precipitation (0.67 ± 0.15 ml L^{-1}).

A 16-month time series of $\delta^{15}N$ values of open-area precipitation and surface runoff are given in Fig. 2. Generally, the range of $\delta^{15}N$ values of atmospheric deposition in the unforested part of BR was quite wide, from, 0.8 ‰ to -15.5 ‰ (Tab. 3). The range of $\delta^{15}N$ values of runoff was narrower (0.5 to -11.1 ‰). The mean $\delta^{15}N$ values of NO_3^- and NH_4^+ deposited in an open area, close to the site of the peat porewater study, were -6.3 ± 0.7 and -6.6 ± 1.0 ‰, respectively, and were statistically indistinguishable ($p > 0.05$). In contrast, the mean $\delta^{15}N$ values of NO_3^- and NH_4^+ of runoff (means of 2.7 ± 0.7 and 2.0 ± 1.3 ‰, respectively) were both significantly heavier than those of the atmospheric input ($p < 0.05$). The $\delta^{15}N$ values of runoff NO_3^- and runoff NH_4^+ were indistinguishable ($p < 0.05$).

Mean concentrations of NO_3^- and NH_4^+ in spruce canopy throughfall (200 m from the peat porewater experimental site) were 3.5 ± 1.8 and 0.2 ± 0.05 mg L^{-1}, respectively. Mean $\delta^{15}N$ values NO_3^- and NH_4^+ in throughfall were -5.1 ± 0.8 and -7.4 ± 1.0 ‰, respectively.

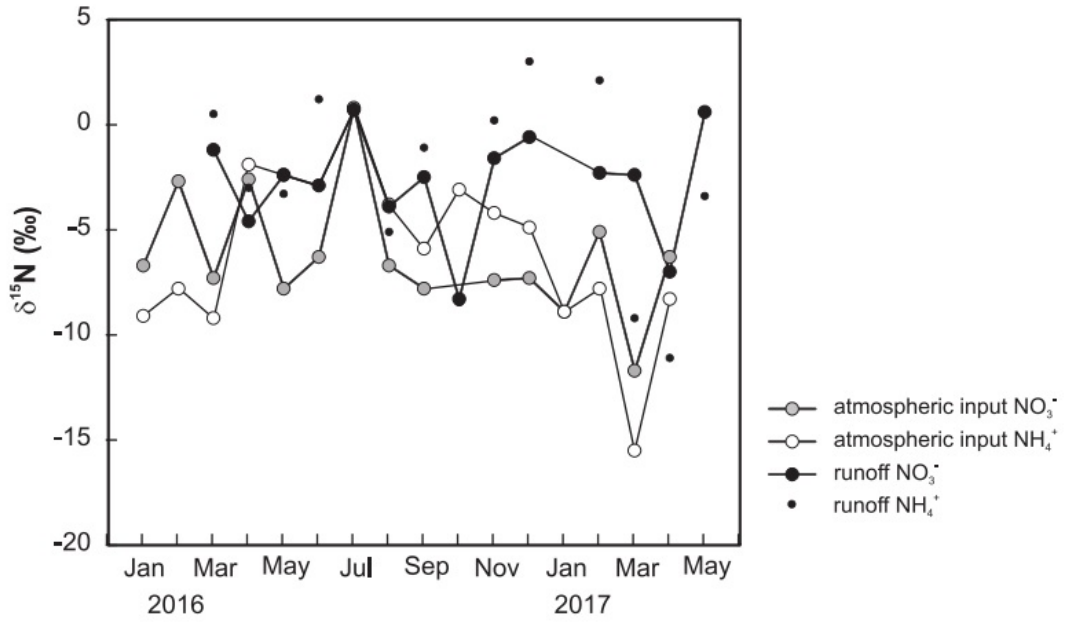


Fig. 2. A time-series of N isotope composition of nitrate and ammonium in atmospheric input and surface runoff from the BR peat bog. Export of both NO_3^- and NH_4^+ contained isotopically significantly heavier N, compared to atmospheric deposition.

3.2. Downcore trends in N concentration in solid peat

Three vertical peat cores from BR exhibited similar N concentration trends, but within-site variability increased with an increasing peat depth (Fig. 3). Downcore, total N concentration first increased (topmost five samples). Below the depth of 17 cm, N concentrations decreased to levels similar to the topmost sample (0.75 wt. % dry mass). Across all studied depths, the mean N concentration was 1.13 ± 0.05 wt. %.

3.3. Nitrate and nitrous-oxide concentrations in peat porewater

Nitrate concentrations in BR porewater were on average lower than in the 2016-2017 atmospheric deposition (means of 0.97 ± 0.06 and 1.8 ± 0.57 mg L^{-1}, respectively; Fig. 4a; Tab. 4). Nitrogen concentrations in BR porewater were mostly also lower than in runoff (0.97 ± 0.06 and 1.6 ± 0.66 mg L^{-1}, respectively). With an increasing peat depth, porewater NO_3^- concentrations first slightly decreased (from 1.0 ± 0.11 to 0.76 ± 0.12 mg L^{-1}), but then increased sharply to a mean value of 1.4 ± 0.20 mg L^{-1} at a depth of 60 cm, which was close to the NO_3^- concentration in runoff (Fig. 4a).

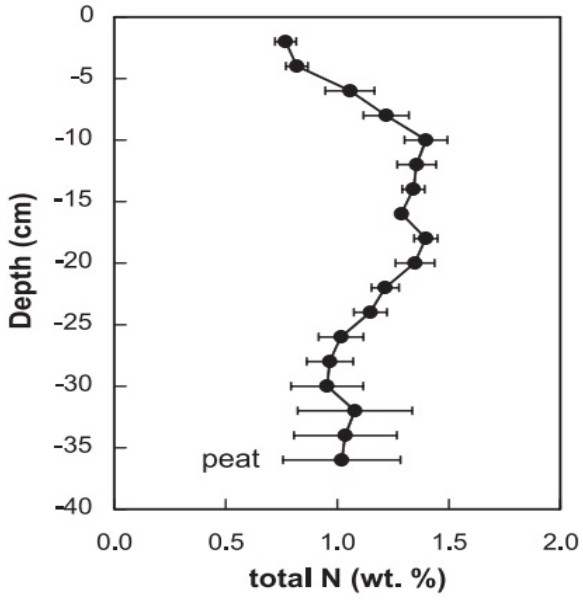


Fig. 3. Vertical trends in the concentration of total N in replicated peat cores from BR (*n* = 3). Means and standard errors are given.

Also N_2O concentrations in porewater gas were lower, compared to N_2O concentrations in the atmosphere (Fig. 4b; Tab. 5). The mean N_2O concentration in the atmosphere 2 m above the wetland was 327 ± 4 ppb, nearly identical the global mean of 328 ppb (IPCC, 2017). The mean N_2O concentration in BR porewater was 271 ± 3 ppb, ca. 18 % lower than in the atmosphere. Slightly lower N_2O concentrations were detected at the 30 cm depth, but the N_2O porewater concentrations were statistically indistinguishable along the vertical profile ($p > 0.05$). With an increasing depth, variability in N_2O concentrations increased (Fig. 4b).

Table 4. Concentration and $\delta^{15}N$ values of pore-water N_2O along vertical profiles through Sphagnum-dominated peat bog BR (Czech Republic).

	N_2O											
Peat depth (cm)	**concentration (mg L^{-1})**						**$\delta^{15}N$ (‰)**					
	1*	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
10	268	274	269	256	280	273	0.7			0.5		
20	277	285	248	274	315		2.0	-0.2	0.3			
30	228	241	271	258	278	272	-1.1	-0.8		0.2		0.3
40	254		251		267	316	-0.5		-1.0		0.1	-9.7
50	253	303	249	249		320	0.6	-14.1	-2.5	0.4		-9.4
60	247	366	238	246	274		-1.3	-20.7	-2.9	-1.1		

**replicate number*

3.4. $\delta^{15}N$ values of porewater NO_3^- and N_2O

Sampling of NO_3^- and N_2O from peat porewaters was performed using different methodology and different equipment (*see* Section *2.2.*). The unplanned drought toward the end of the 23-day porewater-reequilibration period prior to N_2O sampling, followed by an extreme precipitation event on day 24, led to different characteristics of N_2O and NO_3^- samples from the topmost peat layers. The water table sank below the 10 cm depth of the topmost installations only in week 3. The $\delta^{15}N$ values of porewater N_2O thus covered two thirds of the 23-day interval. In contrast, lysimeters designed to sample NO_3^- were activated only on day 19, *i.e.,* at a time when the topmost depth of 10 cm was already above the water table. It follows that the deeper four levels (30, 40, 50 and 60 cm) were water-saturated throughout the experiment, and $\delta^{15}N$ values of NO_3^- and N_2O can be evaluated jointly. In contrast, NO_3^- samples from the 10-cm depth represent only the streamflow of day 24, and cannot be directly compared to the pre-storm samples of N_2O from the same shallow depth.

Accordingly, porewater N_2O and NO_3^- data in Fig. 5 have been color-coded; solid symbols and full lines refer to continuously waterlogged levels, whereas open symbols and dotted lines mark samples incomparable due to drought that was followed by a major precipitation event.

In the deepest sampled level of 60 cm, the mean $\delta^{15}N$ value of porewater NO_3^- (-3.2 ± 1.7 ‰) was higher than the mean $\delta^{15}N$ value of porewater N_2O (-4.3 ± 4.3 ‰; Fig. 5; Tab. 4), but the difference was statistically insignificant ($p > 0.05$). Upcore, starting at the depth of 50 cm, mean $\delta^{15}N$ values of NO_3^- decreased, while mean $\delta^{15}N$ values of N_2O increased (Fig. 5; Tab. 5). A strong negative correlation between these two variables was observed across the 60 to 30 cm depth interval ($p < 0.05$; Fig. 6). At depths shallower than 30 cm, the mean $\delta^{15}N$-N_2O values continued to smoothly increase up to 2.0 ‰, a value slightly higher than the N_2O isotope signature of local atmosphere (down arrow in Fig. 5 top right). The two topmost mean $\delta^{15}N$-NO_3^- values were by 3 ‰ higher than that at the 30-cm depth. These two topmost $\delta^{15}N$-NO_3^- values were very close to the NO_3^- isotope signature of atmospheric input (down arrow in Fig. 5 top left).

Table 5. Concentration and $\delta^{15}N$ values of pore-water NO_3^- along vertical profiles through Sphagnum-dominated peat bog BR (Czech Republic).

	NO_3^-											
Peat depth (cm)	**concentration (mg L^{-1})**						**$\delta^{15}N$ (‰)**					
	1*	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
10		0.89	0.90	0.80	0.80		-12.7	-6.0	-6.6	-7.7	-4.8	
20	0.44		0.60			0.44	-5.2	-5.5	-6.0	-5.6	-6.4	-3.1
30		0.44		0.90	0.90	0.44	-10.5	-4.9	-9.1	-7.7	-14.8	-9.9
40	0.44	0.93	0.40	0.80	0.80		-7.5	-5.7	-13.7	-3.3	-9.8	-8.1
50	0.75		0.89	0.60	0.60		-1.2	-5.1	-0.1	-9.9	0.6	-3.3
60	0.44						-2.9	--3.2	-8.2		-4.4	

3.5. Porewater $\delta^{18}O$-H_2O values

All $\delta^{18}O$ values of peat porewater were between -7.4 and -10.1 ‰ (Tab. 6). The mean $\delta^{18}O$-H_2O value across all depths was -9.0 ± 0.1 ‰. The mean $\delta^{18}O$-H_2O values at individual depths differed by less than 1 ‰ and were statistically indistinguishable ($p > 0.05$; Fig. 4c).

δ^{18}O-H_2O values of runoff were measured on June 8 and July 11, 2017 (-10.1 and -8.7 ‰, respectively), giving an average of 9.4 ‰ (Fig. 4c bottom).

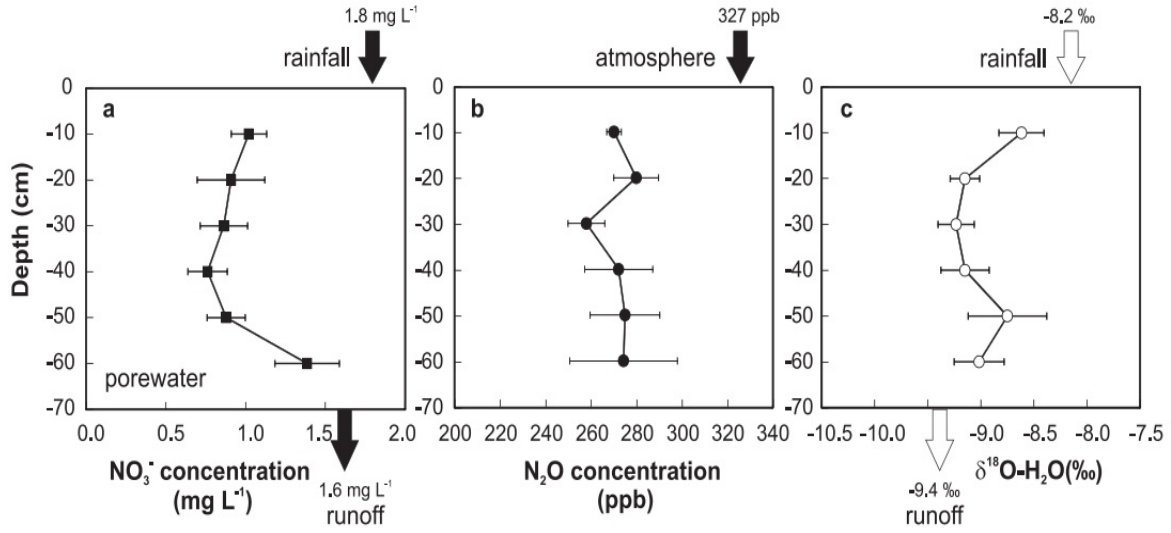


Fig. 4. Reactive nitrogen compounds and water oxygen isotopes in BR peat pore water, early summer 2017. (a) NO_3^- concentrations; (B) N_2O concentrations; (c) δ^{18}O-H_2O values. Means and standard errors are given. Down arrows mark atmospheric inputs and surface runoff.

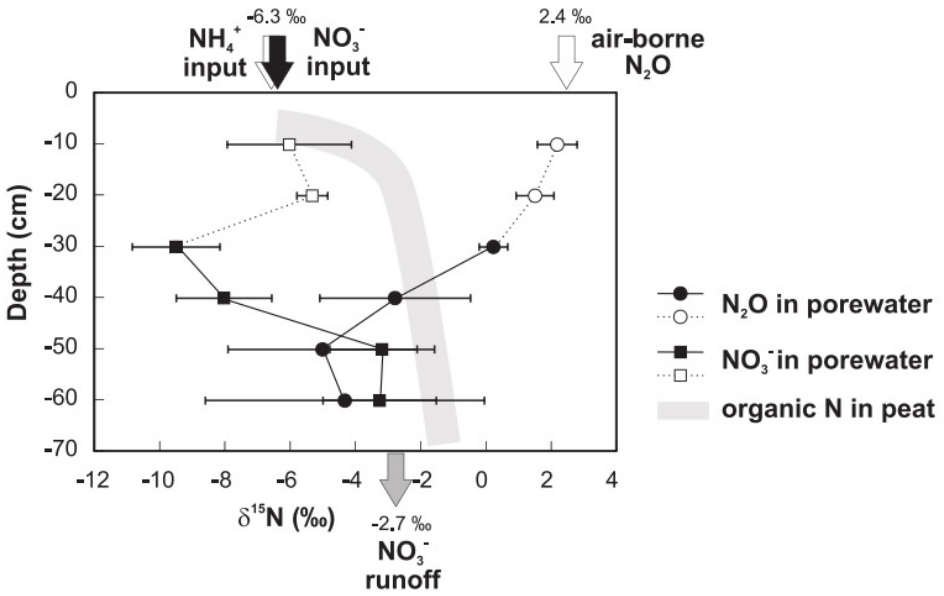


Fig. 5. Nitrogen isotope ratios *vs.* depth plot for BR peat. Solid symbols – permanently water-saturated peat layers; open symbols – topmost peat layers, to various extent affected by a late June dry period accompanied by a short water table drawdown to -15 cm. Means and standard errors are given. Down arrows mark N isotope signatures of atmospheric input

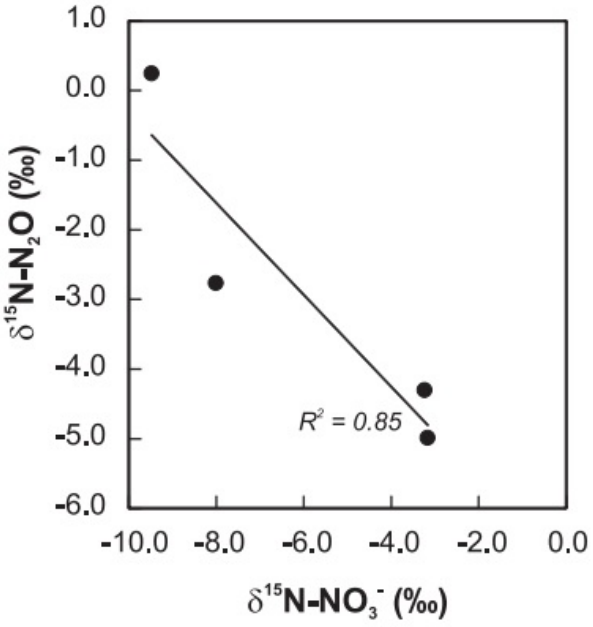
and surface runoff. Grey band representing $\delta^{15}N$ values of bulk solid peat is a compilation from Novak et al. (2014, 2016).

Table 6. $\delta^{18}O$ values of pore water along vertical peat profiles, BR (Czech Republic).

Depth (cm)	**$\delta^{18}O$-H_2O (‰)**					
	1*	**2**	**3**	**4**	**5**	**6**
10	-9.3	-8.9	-7.8	-8.6	-8.8	-8.3
20	-9.0	-8.9	-8.8	-9.1	-9.4	-9.7
30	-9.1	-8.9	-8.9	-9.0	-9.6	-9.9
40	-8.9	-9.1	-9.1	-8.4	-9.3	-10.1
50	-9.3	-8.7	-7.4	-8.4	-8.6	-10.1
60	-9.6	-8.8	-9.0	-8.4	-8.5	-9.8

**replicate number*

Fig. 6. Negative correlation between $\delta^{15}N$-NO_3^- and $\delta^{15}N$-N_2O values in peat pore waters. *See* text for details.



4. Discussion

4.1. Methodological limitations

Nitrate in peat bogs, both primary (deposited from the atmosphere) and secondary (derived from organic matter/ammonium *via* nitrification), is a direct precursor of N_2O. Whereas N_2O produced in wetlands by denitrification has been extensively studied by means of stable isotope ratios, no $\delta^{15}N$ data on peat porewater nitrate have been reported thus far. Methodological difficulties can explain this imbalance. At NO_3^- concentrations of less than 1 mg L^{-1} (Tab. 5), one liter of porewater is needed for analysis (*e.g.,* Bremner, 1965; *cf.,* Huber et al., 2011). In principle, NO_3^- could be extracted from frozen peat cores. However, assuming a common coring diameter (10 cm) and sectioning interval (2 cm), at least 30 peat cores would be needed for a single $\delta^{15}N\text{-}NO_3^-$ analysis. Replicated studies would be unfeasible. Instead, we used suction lysimeters with a five-day sampling interval. This approach made it possible to obtain vertical trends in $\delta^{15}N\text{-}NO_3^-$ in pore water, but we had to compromise on spatial resolution. Suction cups, typically used in upland soils, are known for a poorly defined volume of soil solutions which they actually sample. It is likely that each lysimeter collected soil solution from a larger volume than each soil gas sampler. Significantly different $\delta^{15}N\text{-}NO_3^-$ values were found at several adjacent depths (*e.g.,* 50 and 40 cm; Fig. 5). We therefore suggest that solution volumes sampled at our 10-cm peat depth intervals provided meaningful, vertically stratified $\delta^{15}N\text{-}NO_3^-$ data.

4.2. Contrasting N_r inputs and outputs at the wetland scale

Pollutant N can be transported over long distances due to relatively long residence times of NO_3^- and NH_4^+ in the atmosphere (5-15 days; Galloway et al., 2004). $\delta^{15}N$ values of co-existing NO_3^- and NH_4^+ in atmospheric deposition fingerprint N sources, but can also record N isotope fractionations occurring during transport to the receptor site (Savard et al., 2017). Kendall and Mc Donnell (1998) summarized the reasons for typically more negative $\delta^{15}N\text{-}NH_4^+$ values, compared to $\delta^{15}N\text{-}NO_3^-$, in atmospheric deposition. Biogenic gaseous NH_3, a precursor of aqueous NH_4^+, contains isotopically light N. Industrial NO_x, a precursor of NO_3^-, contains isotopically heavy N (up to 26 ‰), especially if emitted from coal-fired power

stations (Felix et al., 2015, 2017). The overall $\delta^{15}N$ isotope signature of air-borne NO_3^- can be driven to lower positive, or even negative values by an admixture of NO_x emissions from vehicles (down to -13 ‰; Redling et al., 2013).

Data in Tab. 3 and Fig. 5, collected in 2016-2017, along with previously published data from sites located close to BR, make it possible to characterize a temporal change in the N isotope signature of atmospheric input. The oldest N isotope data from 1995-1997 gave a positive mean $\delta^{15}N$-NO_3 value of 1.5 ‰ (Buzek et al., 1998). A second data set comes from 2013, with a negative mean $\delta^{15}N$-NO_3 value of -8.5 ‰ (Novak et al., 2016). The current study yielded also a negative mean $\delta^{15}N$-NO_3 value of -6.3 ‰ in 2016-2017. It appears that with easing atmospheric pollution, open segments of peat bogs in the northwestern Czech Republic received a greater proportion of traffic-derived NO_3^- at the expense of coal-burning derived NO_3^-. The mean $\delta^{15}N$-NH_4^+ values of atmospheric deposition in an open area were -9.0, -8.5 and -6.6 ‰ in 1995-1997, 2013, and 2016-2017, respectively (Buzek et al., 1998, Novak et al., 2016, and the current study). This trend toward higher $\delta^{15}N$-NH_4^+ values probably reflects a change in the source area or in land use.

Mean NO_3^- concentrations of atmospheric input and of stream output were nearly the same and thus provided no insights into within-bog N cycling. By contrast, NO_3^--N in the stream output was isotopically significantly heavier than the input (a 3.6 ‰ shift to less negative $\delta^{15}N$ values). Figs. 2 and 5 thus clearly showed that NO_3^- in runoff was predominantly secondary, *i.e.,* newly formed following organic N cycling in the peat bog. Interestingly, the mean $\delta^{15}N$ value of the atmospheric input was very close to that of the 10-cm deep peat pore water, and the mean $\delta^{15}N$ value of runoff was nearly identical to that of the deepest analyzed peat pore water (Fig. 5). During several hours before cumulative NO_3^- sampling by suction cups, a rain event caused a rapid rise of the bog water table from 15 to 5 cm below *Sphagnum* capitula. The N isotope systematic confirmed that the 10-cm deep NO_3^- sample was derived from fresh rainwater, and, because of its extremely short within-bog residence time, it was not affected by organic N cycling, including nitrification or denitrification. We did not measure the NO_3^--N isotope signature of peat pore water at depths between 70 and 200 cm, but hydrological literature agrees that hydraulic conductivity in mountain-top peat bogs sharply decreases with an increasing depth and that runoff is predominantly generated at shallow depths. Nitrogen isotopes suggest that peat depths of approximately 60 cm below

surface may have significantly contributed to runoff generation at the time of sampling. This conclusion is corroborated by similar $\delta^{18}O\text{-}H_2O$ values of the 60 cm depth pore water and of runoff (a difference of mere 0.5 ‰; Fig. 4c).

4.3. N cycling through Sphagnum and solid peat

Tab. 7 summarizes temporal changes in atmospheric N deposition at Jezeri (JEZ), a site similar to BR, also situated in the northern Czech Republic. At JEZ, monthly hydrochemical input–output mass balances have been constructed for the past 24 years (Oulehle et al., 2017). Atmospheric deposition of total N_r in unforested parts of JEZ was 12.7, 17.5 and 8.6 kg ha^{-1} yr^{-1} in 1995, 2000 and 2015, respectively. According to Lamers et al. (2000), sites receiving < 10 kg N_r ha^{-1} yr^{-1} can be viewed as low-polluted, sites receiving 10 to 18 kg N_r ha^{-1} yr^{-1} are medium-polluted, and sites receiving > 18 kg N_r ha^{-1} yr^{-1} are highly polluted. *Sphagnum* at low- and medium-polluted sites functions as an efficient N filter, and under water-saturated conditions N is not leached to depth greater than 5-10 cm below surface. BR can be currently viewed as a low-polluted site where incoming N is immobilized close to the moss surface. Clearly, at times of a water-table drawdown, rainfall N rapidly reaches all peat layers above the water table depth (15 cm on June 22, 2017)

In the topmost 10 cm, total N concentrations in bulk BR peat systematically increased (Fig. 3). This increase is typical of most *Sphagnum*-dominated peat bogs, regardless of the timing of peak atmospheric N pollution (today *vs.* decades ago), and indicates a certain limited degree of vertical N mobility, accompanying rapid degradation of labile organic compounds in recent plant necromass (see, *e.g.,* Fritz et al., 2014 for discussion). In this study, we did not determine $\delta^{15}N$ values of bulk peat. The grey band in Fig. 5 marks a range of typical $\delta^{15}N$ values of bulk peat in the Czech mountains, based on 150 $\delta^{15}N$ measurements within eight different depth profiles at sites similar to BR, separated into 2-cm vertical segments (similar altitude, N pollution history, and climate; Novak et al., 2015, 2016). The $\delta^{15}N$ values of bulk peat (99 wt. % organic N) rapidly increased to the depth of 15-20 cm, and continued to increase more slowly toward the bottom of the peat cores. The shift toward heavier organic N in deeper peat layers, but also in deeper horizons of aerated upland soils, has been interpreted by numerous authors as resulting from preferential mineralization and mobilization of isotopically light N (Nadelfoffer and Fry, 1988). The residual isotopically heavier N remains

in the maturating peat substrate. Importantly, typical residual peat substrate at a depth of 40 to 60 cm, where maximum denitrification rates have been described in other peat bog studies (Goldberg et al., 2008, and references therein), contains isotopically heavier N, compared to NO_3^--N and N_2O-N at BR (Fig. 5 bottom). Nitrogen isotope systematics thus give an intrinsically consistent picture: Nitrification and denitrification remove from the 60- to 40-cm deep peat N that is isotopically lighter than N of the residual organic matter.

Table 7. Atmospheric deposition fluxes of reactive nitrogen forms in the vicinity of Brumiste (BR). Data from catchment Jezeri, Ore Mts. (Oulehle, 2018)

Site	1995				2000				2015			
	open-area precipitation		canopy throughfall		open-area precipitation		canopy throughfall		open-area precipitation		canopy throughfall	
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
	kg ha^{-1} yr^{-1}											
JEZ	7.0	12.7	11.4	13.6	10.0	7.5	15.6	16.8	5.8	2.8	5.0	4.2

4.4. Scavenging of air-borne N_2O by the wetland

Ombrotrophic peat bogs can function as a source or a sink of N_2O (Chapuis-Lardy et al., 2007). Under acidic conditions (mean BR bog water pH of 4.2; Tab. 2), nitrification is a generally slow process (Zhu et al., 2013), and large N_2O emissions are not expected. This is in a sharp contrast to higher-pH minerotrophic fens from which sizeable N_2O emissions have been observed (Goldberg et al., 2009). A comparison of atmospheric and porewater N_2O concentrations alone (Fig. 4b) permits a conclusion important in the broader context of atmospheric N_2O budget. N_2O concentrations in the porewater profile (mean of 275 ppb) were significantly ($p < 0.05$) lower than the local N_2O concentration in the air (327 ppb). Hence, it is unlikely that BR was a net source of N_2O at the time of our study. Instead, N_2O may have been removed from the atmosphere, entering the wet soil along a concentration gradient, and, to some extent, microbially reduced in the porewater. Indeed, in our previous study in the Eagle Mts. (northeastern Czech Republic; Novak et al., 2015) we measured "negative" N_2O emissions from an ombrotrophic *Sphagnum* bog on one sampling day, and negligible positive N_2O emissions (< 0.02 μmol m^{-2} h^{-1}) on a second sampling day. The previously studied bog in the northeast was not a source of N_2O despite the fact that the N_2O concentrations in the 60-cm deep porewater were 70 times higher than at BR, and despite

significantly higher atmospheric N_r inputs due to higher industrial pollution, compared to BR.

Scavenging of atmospheric N_2O by BR wetland was corroborated by the similarity of N_2O-N isotope signature in the shallowest porewater depths and in the atmosphere (both close to 2 ‰; Fig. 5).

4.5. The role of denitrification at BR

From the atmosphere/peat surface to the depth of 50 cm, the mean $\delta^{15}N$ value of N_2O relatively smoothly decreased ($p < 0.05$; Fig. 5), while N_2O porewater concentrations remained constant (statistically insignificant differences among individual depths, $p > 0.05$; Fig. 4b). Given such a combination of concentration and isotope patterns, the decreasing $\delta^{15}N$-N_2O values downcore cannot be explained without invoking denitrification. We are not aware of any experimental data on N isotope effects of N_2O diffusion in a water column, but N_2O containing isotopically light N might be associated with a higher diffusion rate. If so, the diffusion front at greater depth would have a lower $\delta^{15}N$ value, in agreement with Fig. 5. At BR, however, diffusion to greater depths was unlikely because of the non-existence of a within-peat N_2O concentration gradient (Fig. 4b). On the other hand, a small rate of *in-situ* denitrification could be consistent with both the N_2O concentration and N_2O-N isotope pattern observed in the porewater. In such a scenario, N_2O is both added to, and consumed at, each depth between 30 and 50 cm. The low concentrations of the NO_3^- reactant (≤ 1 mg L^{-1}) in BR peat porewater (Fig. 4a) themselves do not preclude the process of denitrification; in our previous study, we found a rain-fed bog with < 1 mg NO_3^- L^{-1} in porewater, producing as much as 140 ppm N_2O (more by a factor of 500, compared to BR; Novak et al., 2015). We assume a dynamic character of the small NO_3^- pool in peat porewater, replenished by nitrification and dispersion/diffusion of atmospherically deposited NO_3^-, and depleted by reduction to N_2O. Simultaneously, the small N_2O pool in pore water (mainly between depths of 50 and 30 cm), continuously replenished by denitrification, is depleted by further reduction to N_2. It is the N_2O reduction to N_2 that leaves behind isotopically heavier residual N_2O-N, seen upcore in Fig. 5 (lower part). Mixing of this residual N_2O with atmospheric N_2O, more intense in the shallowest peat layers, is needed to explain the relatively stable N_2O concentrations along the vertical porewater profile.

We suggest that the significantly increasing mean $\delta^{15}N$ value of NO_3^- from the 30 to 50-cm depth ($p < 0.05$; Fig. 5) is also related to denitrification. Nitrate at the 30-cm depth was isotopically different from atmospheric NO_3^- (on average by -3.6 ‰ lighter). It clearly contained some secondary NO_3^-, resulting from nitrification. With an increasing peat depth, isotopically heavier NO_3^--N probably reflects higher rates of denitrification. Previous studies have indicated that the 50-60 cm depths in waterlogged organic soils may be associated with the highest denitrification rates (Goldberg et al., 2009); these layers are effectively anoxic and, unlike deeper/older peat, still abound in labile organic C. At a depth of 50 cm, more advanced denitrification left behind isotopically heavier N of residual NO_3^-, compared to the 30-cm depth. Depending on temperature and chemistry, peat porewater contains at least 100 times more NO_3^--N than N_2O-N per unit volume. Given that 1mole of NO_3^- produces similar to 1 mole of N_2O during denitrification, the N isotope signature of the NO_3^- pool at a particular depth is more robust than that of N_2O. Yet, we have seen in Fig. 6 that there was a strong negative correlation ($R^2 = 0.85$, $p < 0.05$) between $\delta^{15}N$-NO_3^- and $\delta^{15}N$-N_2O values in the BR porewater. Between the depths of 30 and 50 cm, the N isotope shifts in NO_3^- and N_2O were of very similar magnitude (-6 and +5 ‰, respectively). We do not have sufficient data to construct an N isotope mass balance, but it is obvious from the discussion above that this negative relationship (solid symbols in Fig. 5) could not be a result of a single process. Laboratory studies have shown that N_2O, as a product of nitrification, can contain N that is isotopically lighter by up to 40 ‰, compared to NO_3^--N. At BR, we observed isotopically lighter N_2O-N, compared to NO_3^--N only at the depths of 50 and 60 cm, however, the difference between both mean $\delta^{15}N$ values was statistically insignificant. In our previous study (Novak et al., 2015) with much more vigorous N_2O production than at BR, we observed even heavier mean N_2O-N in peat porewater (0 to 2 ‰, as opposed to -4 to 0 ‰ at BR–solid symbols). In the cited previous study, partial reduction of porewater N_2O to N_2 was the only feasible explanation of isotopically heavier N_2O-N toward shallower depths, in order to reconcile vigorous N_2O production at a depth of 60 cm with negligible N_2O emission from the bog surface to the atmosphere. We conclude that the isotopically heavier N_2O-N toward shallower depths at BR (solid circles in Fig. 5) must have also been a result of partial reduction of N_2O to N_2 as the final step of denitrification.

4.6. The overall effect of the late-June water table drawdown

Fig. 7a shows that high air temperatures persevered only for four days after the activation of the lysimeters, and that the stormflow on June 23, 2017, which caused re-wetting of the top peat layers, was smaller compared to another precipitation event earlier (on June 4). Fig. 7b shows the results of a water table monitoring four years earlier, published by Bohdalkova et al. (2013). The lower curve shows the water table level just a few meters from our N porewater study (*see* Fig. 1 for location of water table monitoring sites). Similar to 2017, a 15-cm water table drawdown was recorded in 2013. The low N_2O concentrations in porewater observed by us in 2017 may be quite common. The upper curve shows completely wet *Sphagnum* at the central part of BR, close to the pond. That segment of the bog is more favourable for CH_4 emissions (Bohdalkova et al., 2013), and may be also more favourable for N_2O emissions.

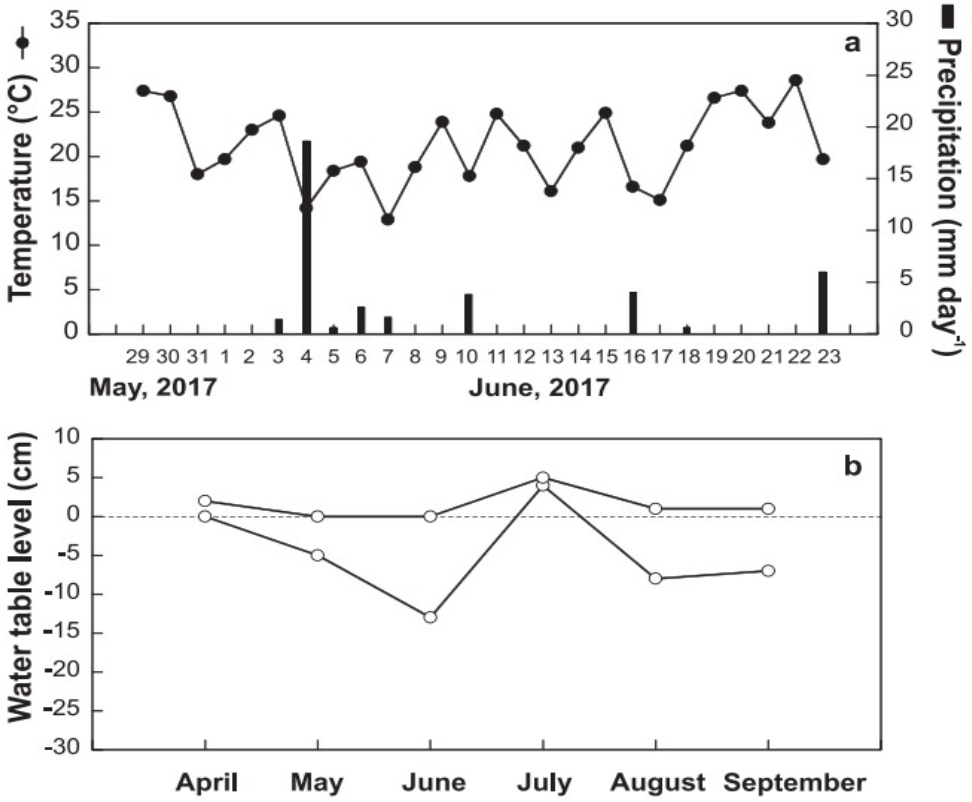


Fig.7. Meteorological parameters of the BR bog. (a) Maximum daily temperatures at the time of porewater and gas sampling (solid circles), and daily rainfall totals (solid columns); data from the Horni Blatna meteorological station, located 4 km from BR at the same elevation; (b) Water table level in the central part of the bog (upper curve), and in the southern part of the bog, close to the site of the N isotope study (lower curve). After Bohdalkova et al. (2013). For monitoring sites location *see* Fig. 1b.

We suggest that the unplanned short water table drawdown toward the end of our field experiment at BR did not affect redox processes taking place deeper than 20 cm below bog surface to an extent which would invalidate our interpretations in Sections *4.4.* and *4.5.* We can support this suggestion by our previous observations of the behavior of another redox-sensitive element, sulfur (S), in rain-fed peat bogs of Central Europe, the U.K. and the U.S. Despite some degree of porewater oxygenation, especially following precipitation events, $\delta^{34}S$ values at practically all study sites started to systematically decrease already in the topmost 2 cm of vertical peat profiles, indicating *anaerobic* bacterial sulfate reduction (Novak et al., 1994, 1999, 2005).

5. Conclusions

For the first time, a combination of N isotope profiles is reported for NO_3^- and N_2O in pore waters of an ombrotrophic peat bog. Unforested segments of the BR peat bog, situated in the northwestern Czech Republic, experienced a period of medium N deposition (18 kg N ha^{-1} yr^{-1}) around the year 2000, but today belong to low-polluted areas (9 kg N ha^{-1} yr^{-1}). Atmospheric deposition in the adjacent spruce stands decreased from 32 to 9 kg N ha^{-1} yr^{-1} over the same period of time. In summer 2017, N_2O concentrations in porewater gas were by 18 % lower than N_2O concentrations in the atmosphere. Consequently, the studied bog was not a source of N_2O for the atmosphere, but rather a sink. Nitrous oxide was scavenged from the air by peat microorganisms and further reduced to N_2, a gas with no warming potential. Between the depths of 50-60 cm below bog surface, the mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N\text{-}N_2O$ values were similar. Upcore, $\delta^{15}N\text{-}N_2O$ increased significantly up to a value identical to the $\delta^{15}N\text{-}N_2O$ in the atmosphere, while the N_2O concentrations were nearly constant throughout the pore water profile. This isotope increase was probably caused by the final step of denitrification, N_2O reduction to N_2. Also upcore, the $\delta^{15}N\text{-}NO_3^-$ values decreased significantly to a depth of 30 cm. In the uppermost peat segments, the $\delta^{15}N\text{-}NO_3^-$ value of pore water became similar to the higher $\delta^{15}N\text{-}NO_3^-$ value of atmospheric deposition. The strong negative correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N\text{-}N_2O$ values found in deeper pore waters (60-30 cm below surface) could not be a result of a single process, NO_3^- reduction to N_2O, because this process is associated with an isotope fractionation toward isotopically lighter, not heavier, product. Instead, upward diffusion/ebullition of the N_2O generated by more efficient NO_3^- reduction in deeper peat layers was probably combined with reduction to

N_2. The residual N_2O became progressively enriched in the heavier isotope ^{15}N. Our study confirmed that ombrotrophic peat bogs are not a major source of the greenhouse gas N_2O for the atmosphere. At the same time, N isotope systematics in BR peat pore water indicated that denitrification proceeded, probably at low rates, even under an acidic pH of around 4.

6. Acknowledgement.

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